Chapter 3
Deposition of Sulfur and Nitrogen Species

This chapter presents information on deposition of sulfur and nitrogen species. The discussion on modeled dry deposition for 1999 is preceded by examples of deposition velocities which are combined with concentration data to estimate fluxes. Wet deposition data obtained from NADP/NTN for 1999 are also presented. The dry and wet deposition data were combined to estimate total deposition of sulfur and nitrogen. In addition, 10-year trends in dry, wet, and total deposition are presented.

Dry Deposition

Dry deposition processes were simulated using the multi-layer model (MLM) described recently by Meyers *et al.* (1998) and Finkelstein *et al.* (2000). The MLM was run using CASTNet meteorological and vegetation data to calculate deposition velocities (V_d) over the 10-year period. A brief description of the MLM is provided in Chapter 1. The modeled deposition velocities were combined with measured ambient concentrations to estimate dry depositions (fluxes) of various sulfur and nitrogen species.

Deposition Velocities

The MLM was run using meteorological measurements and information on land use, vegetation, and surface conditions to calculate dry deposition velocities for SO_2, HNO_3, O_3, and particles. Deposition velocities were calculated for each hour with valid meteorological data for each CASTNet site for the period 1990 through 1999.

Hourly deposition fluxes were calculated as the product of the hourly deposition velocity obtained from the MLM and the corresponding hourly concentration. Hourly concentrations were obtained from the weekly filter pack results; all hourly concentrations during a filter pack sampling period were assumed to be equal to the filter pack sample concentration and constant for the duration of the sample.

Weekly deposition fluxes are the sum of the valid hourly fluxes for a standard deposition week, divided by the ratio of valid hourly fluxes to the total number of hours in the standard week to account for missing or invalid values. A standard deposition week is defined as the 168-hour period from 0800 Tuesday to 0800 the following Tuesday. For some weeks, the filter pack sampling period did not correspond exactly with the standard deposition week, resulting is some deposition weeks being derived from hourly concentrations from more than one filter pack sample. A weekly deposition flux is considered valid if it is comprised of valid hourly values for at least 75 percent of the 168-hour week (i.e., 126 hours).

Similarly, quarterly fluxes are calculated from weekly values, and are considered valid if they are comprised of valid weekly values for at least 8 weeks of the 13-week period. Annual values are calculated from quarterly values, and are considered valid if they are comprised of at least three valid quarters.

Examples of weekly deposition velocities and fluxes for four sites for 1999 are provided to illustrate the products of the MLM simulations. The four sites were selected to characterize a variety of land use and terrain settings and also to provide comparisons to previous versions of the model (EPA, 1998a; ESE, 2000). The Arendstville, PA site (ARE128) is in rolling terrain with nearby peach orchards. The Alhambra, IL site (ALH157) is agricultural (corn, soybean, wheat) in a flat terrain setting. The Coweeta, NC site (COW137) is forested, complex terrain. The Sand Mountain, AL site (SND152) is rolling terrain with predominantly grass and crops.

Figure 3-1 shows weekly average deposition velocities for the four sites. The MLM simulates the highest SO_2 deposition velocities at the rolling agricultural site with values about twice as high as the forested mountainous site. The data show weekly variability up to approximately a factor of 1.5 with no patterns in the simulations. The intersite variability is up to a factor of 3.0. Figure 3-2 shows weekly deposition velocities for HNO_3. The modeled data generally show an annual cycle with higher values in the warmer months. Deposition velocities for particles are shown in Figure 3-3. The MLM simulations show higher values from the spring through the fall with about a factor of 3.0 intersite variability and significant weekly variability. The O_3 deposition velocities (Figure 3-4) show a strong summertime peak with a 200 to 300% increase over winter values. The flat agricultural site in Illinois, ALH157, shows the lowest values.

Tables 3-1 and 3-2 were constructed to present mean values of V_d and to show typical geographic variability. Annual average deposition velocities for SO_2 and HNO_3 are given by subregion for the period 1990 through 1999 in Table 3-1. Table 3-2 summarizes deposition velocities for O_3 and aerosols (SO_4^{2-}, NO_3^-, and NH_4^+) by subregion. The subregions (Figure 3-5) were taken from Holland *et al.* (1998) who performed a statistical analysis of CASTNet SO_2 measurements over the period 1989 through 1995. The median V_d for SO_2 is 0.34 centimeters per second (cm/sec) in the East and 0.23 cm/sec in the West. Eastern velocities are about 50% higher than western values. The SO_2 data show about 50% geographic variability on an annual basis. Annual deposition velocities for HNO_3 are about 1.0 to 1.5 cm/sec. Annual O_3 V_d vary from about 0.18 cm/sec for the eastern sites to about 0.13 cm/sec for the western sites. V_d for particles are about 0.1 cm/sec for the eastern sites and about 0.15 cm/sec for the western sites. In a sense, these annual values illustrate the relative propensities for dry deposition for the four types of pollutants.

The same four sites, ARE128, ALH157, COW137 and SND152, were selected to illustrate weekly distributions of SO_2 deposition rates. Figures 3-6 through 3-9 show time series of weekly SO_2 concentrations, deposition velocities, and fluxes for 1999 for the four sites. ARE128 shows the largest flux, which is the result of relatively high SO_2 concentrations. SND152 and ALH157 also show significant dry deposition. COW137 experiences almost no dry deposition of SO_2 because of the very low measured concentrations.

Sulfur Species

MLM simulations were done separately for SO_2 and SO_4^{2-}. The model calculations were summed to obtain dry deposition estimates of total sulfur (as S) for 1999, which are shown in Figure 3-10. The map shows a narrow region of depositions greater than 5.0 kilograms per hectare (kg/ha) from Kentucky along the Ohio River into New Jersey. Deposition above 5.0 kg/ha was also estimated for SND152. Otherwise, the flux data show strong gradients from the Ohio Valley to New England and also to Wisconsin and northern Minnesota. Depositions for the western sites are all less than 1.0 kg/ha, except for Big Bend National Park, TX (BBE401), and generally less than 0.5 kg/ha. MLM simulations were not done for those sites in Figure 3-10 with no numerical value adjacent to the site location, largely because of incomplete meteorological data.

Figures 3-11 and 3-12 provide maps of 1999 dry depositions of SO_2 and SO_4^{2-}, respectively. Figure 3-13 depicts the percentage of total dry sulfur deposition from SO_2 for 1999. The map shows that SO_2 is the major contributor to dry deposition. The percentage is generally above 75% for most of the eastern sites and approximately 90% for those sites near major sources. Some western sites receive less of their sulfur deposition from SO_2, primarily because of their remote locations and distances from major sources.

Nitrogen Species

Figure 3-14 provides a map of dry fluxes of total nitrate (HNO_3 + NO_3^-, as N) for 1999. Most of the eastern sites have values above 2.0 kg/ha. Nitrate is defined here as nitric acid plus nitrate aerosol for the purpose of estimating dry fluxes. The dry (and later wet) ammonium fraction is not included in the deposition estimates. The CASTNet sites situated along the Appalachians exhibit a complex geographic pattern driven by the distribution of HNO_3 concentrations (see Figure 2-4). The nitrate fluxes estimated for the western sites vary from 0.16 kg/ha in the North Cascades National Park (NCS415) to 2.19 kg/ha at Sequoia National Park (SEK402).

Figures 3-15 and 3-16 provide maps of 1999 dry depositions (as N) of HNO_3 and NO_3^-, respectively. Figure 3-17 shows the percentage of total dry nitrate deposition from HNO_3 for 1999. HNO_3 contributes more than 90% of the nitrate deposition at all but two of the monitoring sites.

Wet Deposition

Estimates of wet depositions were obtained from NADP/NTN measurements from sites nearest CASTNet sites. These NADP/NTN sites were selected even though some sites are greater than 60 km from CASTNet sites. At these distances the wet deposition measurements may not be representative of actual wet deposition at CASTNet sites. Appendix D lists the monitoring sites used in this analysis.

Sulfate

Figure 3-18 presents wet depositions of SO_4^{2-} (as S) measured during 1999. The map shows a large area of wet fluxes greater than 5.0 kg/ha extending from Mississippi to Illinois to New York. The highest wet deposition rates were measured in eastern Ohio. Sharp gradients were observed from Pennsylvania across New England and from Illinois across Wisconsin. Fluxes at the eastern sites were generally lower in 1999 than in 1998 (ESE, 2000). Values at western sites ranged from 1.85 kg/ha at Mount Rainier (MOR409) to 0.09 kg/ha at Lassen Volcanoes National Park, CA (LAV410).

Nitrate

A map of 1999 wet depositions of NO_3^- (as N) is given in Figure 3-19. Many sites in the Midwest to the Mid-Atlantic to southern New York measured fluxes greater than 3.0 kg/ha. The highest deposition rates were observed from eastern Ohio to northwestern Pennsylvania to Ontario. Western sites observed wet depositions from 2.02 kg/ha at Rocky Mountain National Park (ROM406) to 0.15 at LAV410.

Total Deposition

Sulfur Species

Figure 3-20 provides a map of 1999 total sulfur depositions. The map was constructed by adding depositions of dry (Figure 3-10) and wet (Figure 3-18) depositions. For the eastern sites, total sulfur fluxes ranged from a peak of about 15 kg/ha to approximately 3 kg/ha in northern Minnesota. The western sites measured deposition from about 2.27 kg/ha at MOR409 to 0.61 kg/ha in Death Valley, CA (DEV412). Figure 3-21 presents a map with ratios of dry to total sulfur deposition. Ratios ranged from about 0.5 along the Ohio River to 0.2 at monitoring sites distant from major source regions. High-elevation sites also experienced relatively low contributions from dry deposition. NCS415 had the lowest ratio of 0.07.

Nitrogen Species

A map of 1999 total nitrate (wet and dry) depositions is presented in Figure 3-22. The map shows a region with depositions above 5.0 kg/ha from Kentucky to Vermont. A value above 5.0 kg/ha was also observed at SND152. Figure 3-23 provides a map with ratios of dry to total nitrate deposition. Ratios ranged from a low of 0.09 at Woodstock, NH (WST109) to 0.75 at BBE401. More typical values ranged from 0.35 to 0.55.

Ten-Year Trends

One of the goals of CASTNet is to assess trends in depositions. Trends analyses were performed using linear regressions averaged over 34 eastern sites versus the year from 1990 through 1999. Figure 3-24 shows a linear regression based on annual dry depositions of sulfur (SO_2 + SO_4^{2-}, as S). Annual SO_2 emissions for states east of, and including, the north-south line of states from Minnesota to Louisiana are also depicted. The figure shows a significant reduction in composite, annual dry sulfur depositions and a strong relationship with decreases in annual SO_2 emissions.

Figure 3-25 shows the linear regression based on annual dry nitrate (HNO_3 + NO_3^-, as N) depositions over the 10-year period. Annual nitrogen oxides (NO_x) emission data are also plotted. The data show a slight increase in dry nitrate deposition.

Figure 3-26 shows the trend in composite, annual wet sulfate (as S) depositions. The results show a significant reduction in wet deposition over the period and a good relationship with decreases in SO_2 emissions. Figure 3-27 shows the regression of annual wet nitrate (as N) over the 10-year period. No trend is evident in the measurements.

Figures 3-28 and 3-29 show the trends in total (wet + dry) sulfur and nitrate depositions, respectively, over the period 1990 through 1999. Total sulfur deposition shows a significant decrease while total nitrate shows a slight increase.

Figures 3-30 and 3-31 show annual rates of dry, wet, and total sulfur and nitrate depositions, respectively, on the same figures. The two figures illustrate the relative contributions of dry and wet deposition to total deposition. Figure 3-32 shows the year-by-year percentages of total deposition from dry deposition from the composite, annual values. Dry sulfur deposition contributes approximately 40% of total deposition with an annual variation from 35 to 42%. Site-by-site percentages were provided in Figure 3-21. Dry nitrate deposition contributes approximately 37% of total deposition with a variation between 34 and 41%. Dry nitrate site-by-site percentages are provided in Figure 3-23.

Figure 3-1. Weekly Average SO_2 Deposition Velocities for Four Land Use Types (1999)

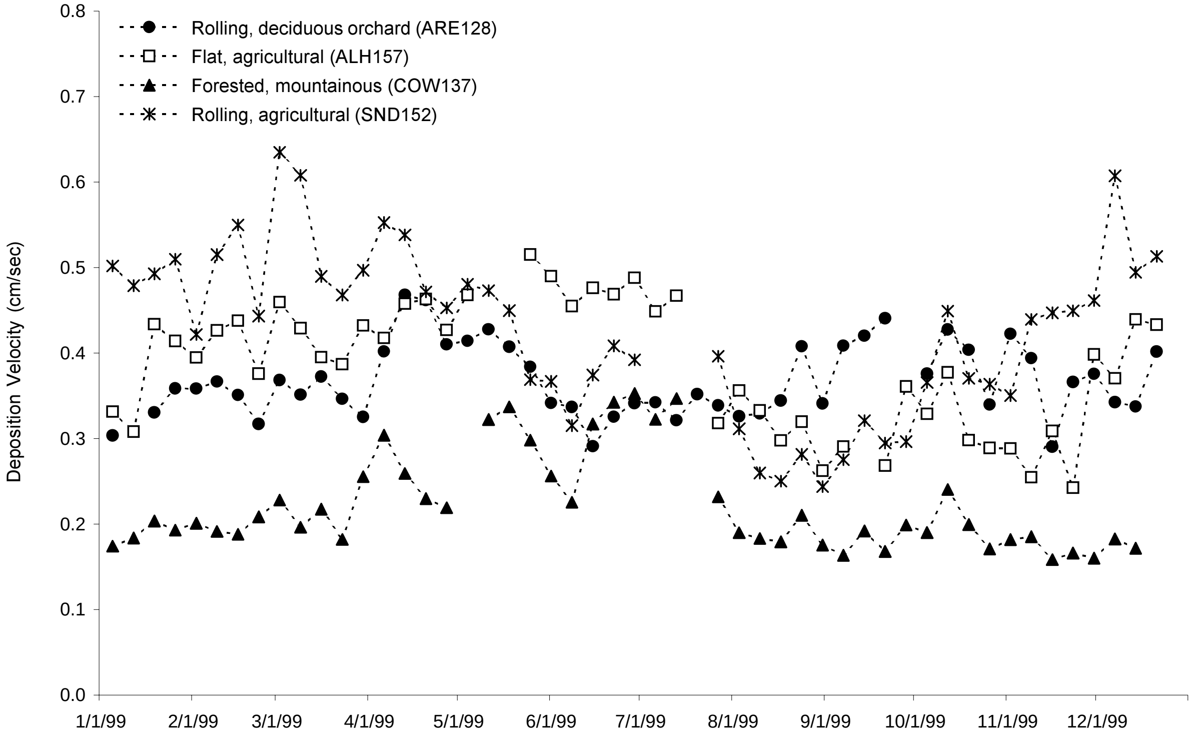


Figure 3-2. Weekly Average HNO_3 Deposition Velocities for Four Land Use Types (1999)

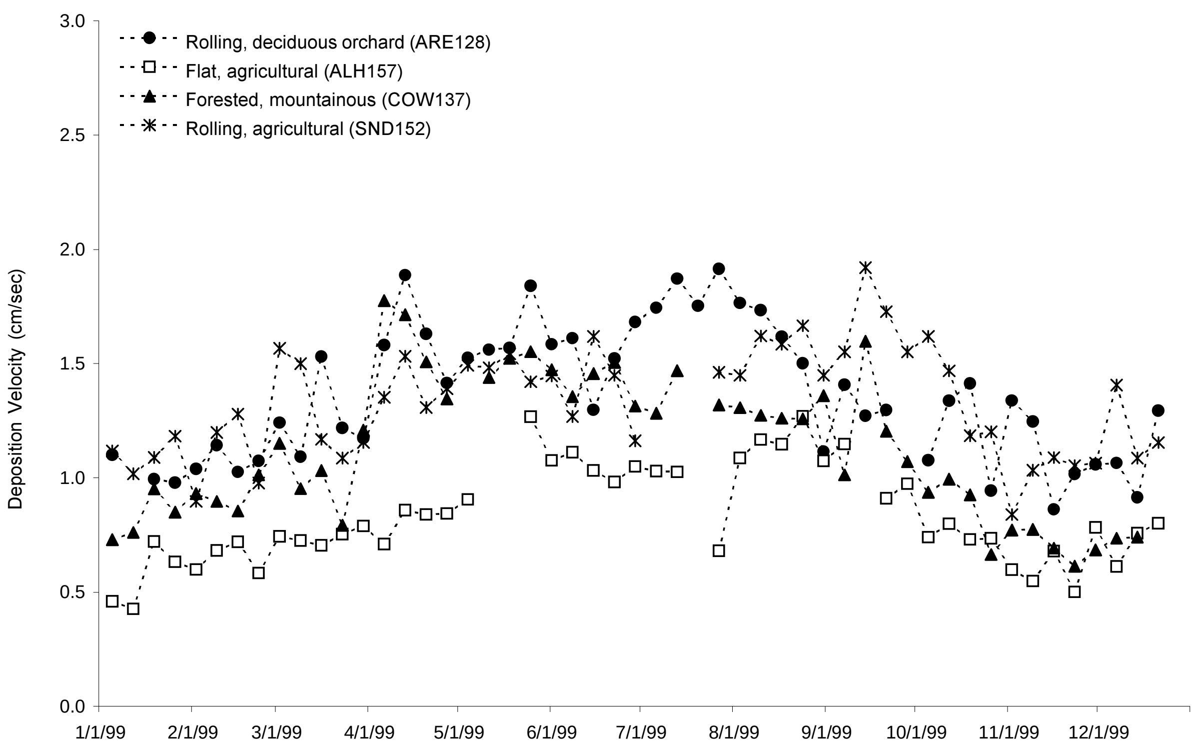


Figure 3-3. Weekly Average Particle Deposition Velocities for Four Land Use Types (1999)

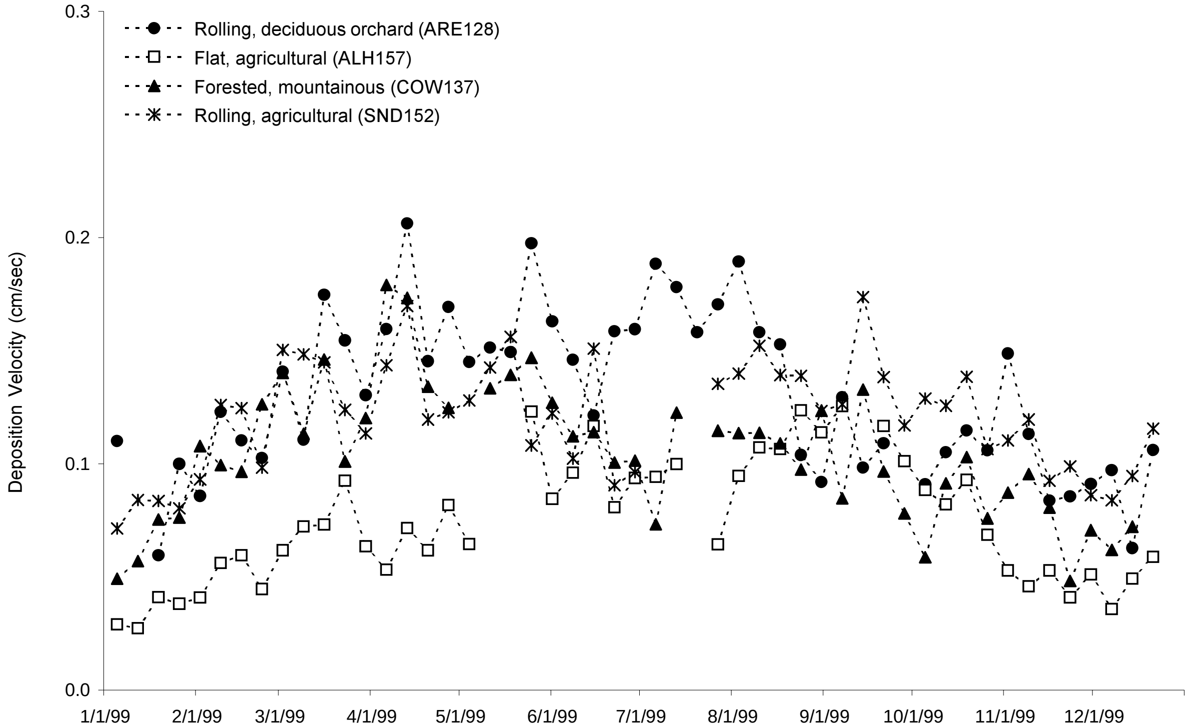


Figure 3-4. Weekly Average Ozone Deposition Velocities for Four Land Use Types (1999)

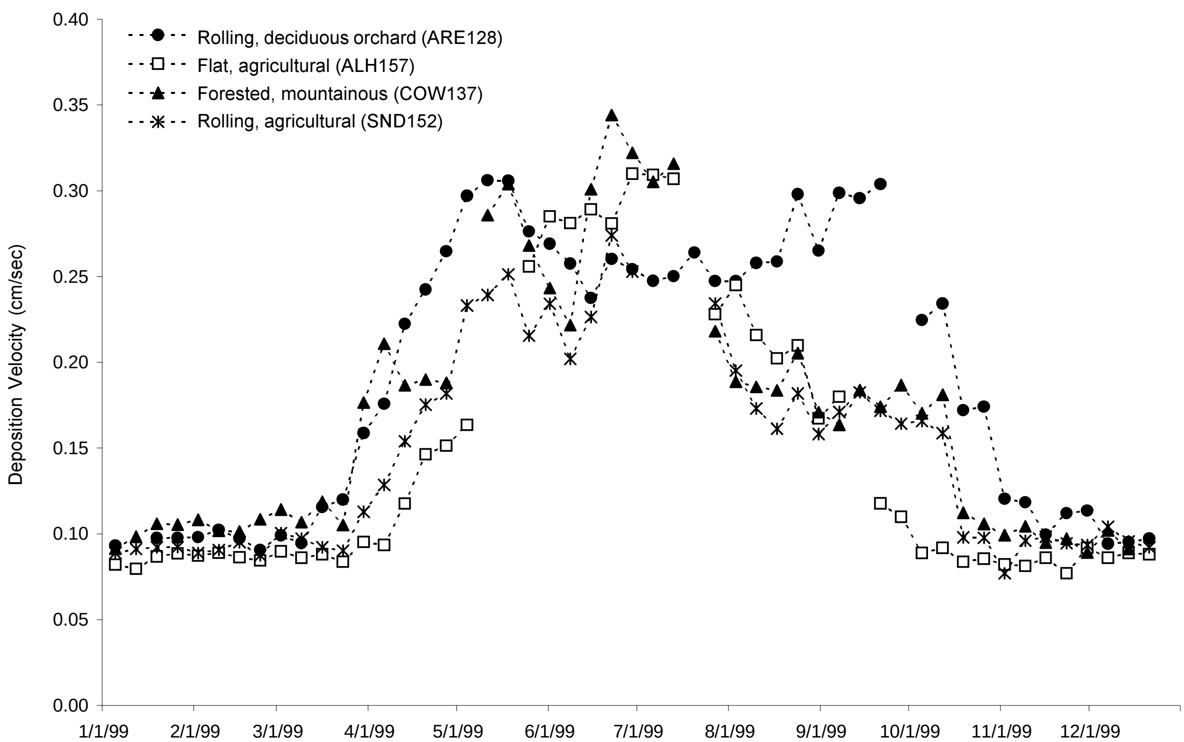


Figure 3-5. Map of Regions for 35 Eastern Sites Used in Regional Analysis

Figure 3-6. Weekly SO_2 Concentrations, Deposition Velocities, and Fluxes for Rolling, Deciduous Orchard (ARE128)

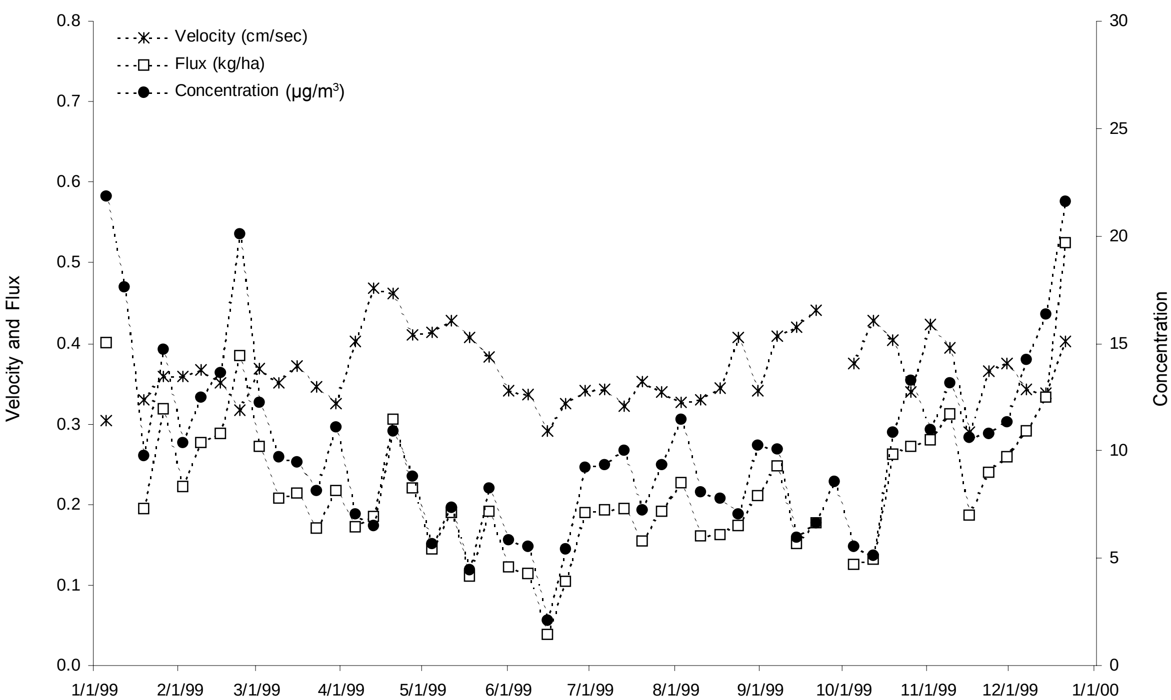


Figure 3-7. Weekly SO_2 Concentrations, Deposition Velocities, and Fluxes for Rolling, Agricultural Site (SND152)

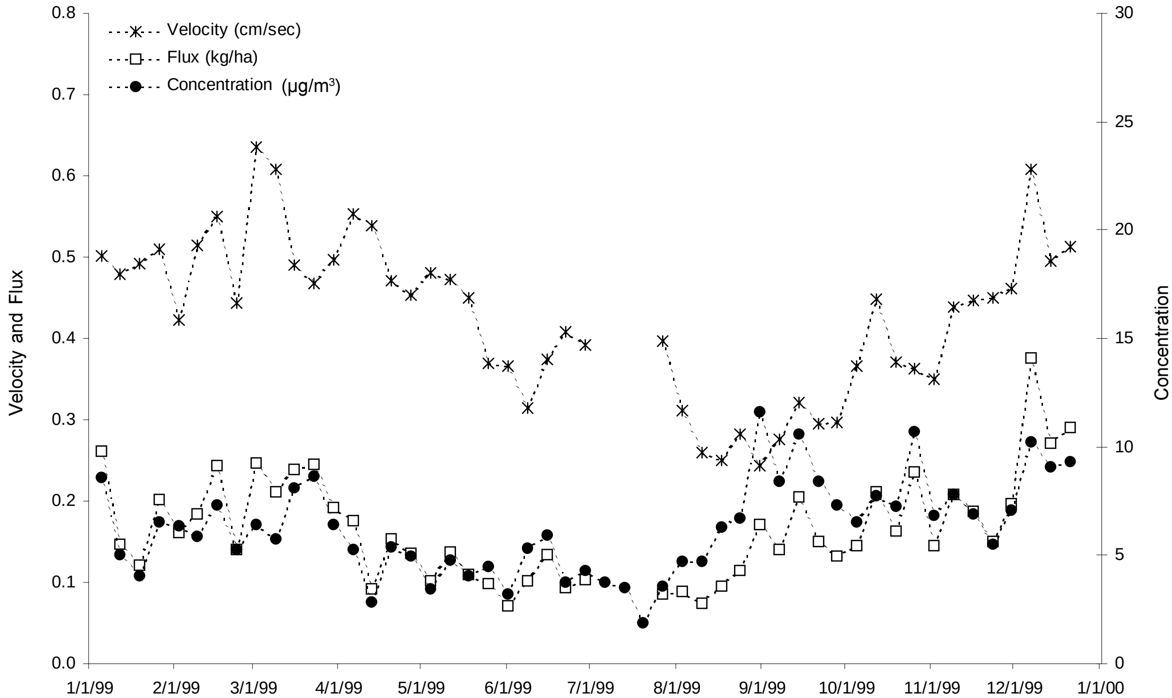


Figure 3-8. Weekly SO_2 Concentrations, Deposition Velocities, and Fluxes for Flat, Agricultural Site (ALH157)

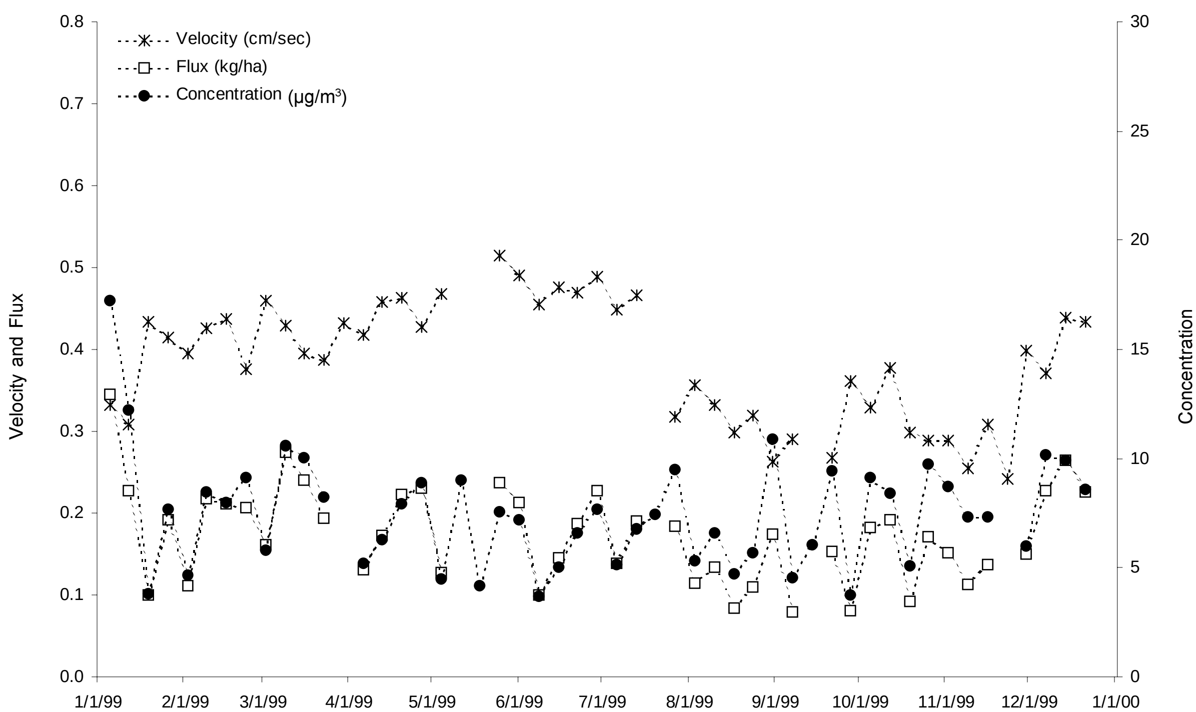


Figure 3-9. Weekly SO_2 Concentrations, Deposition Velocities, and Fluxes for Forested, Mountainous Site (COW137)

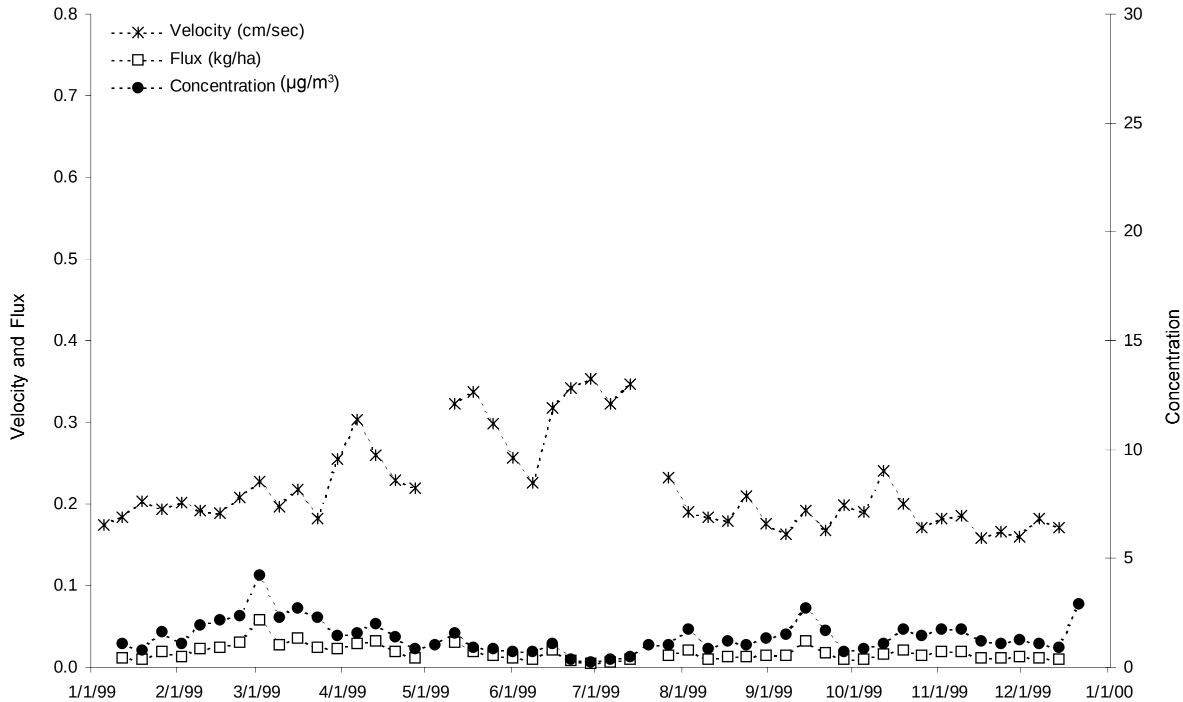


Figure 3-10. 1999 Total Dry Sulfur Deposition (kg/ha)

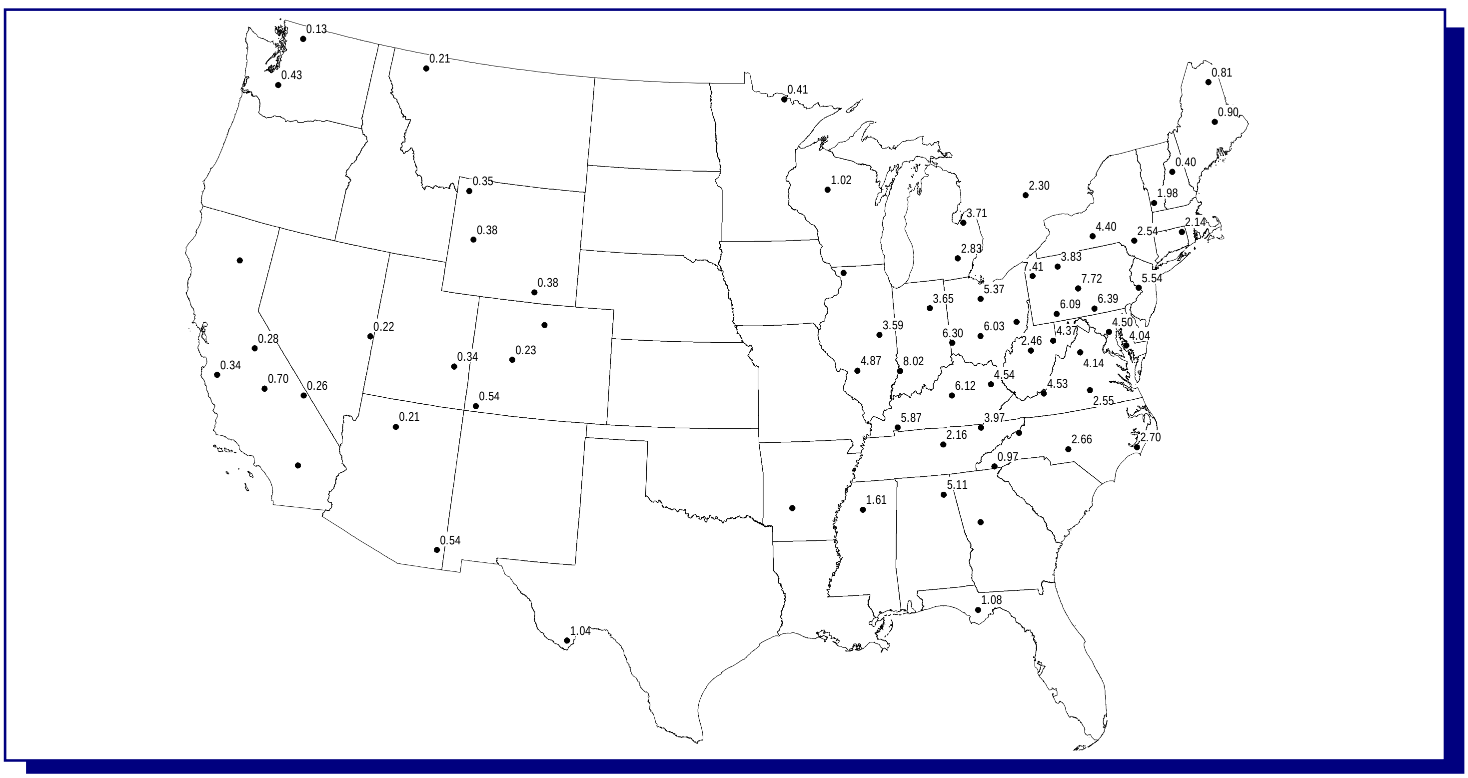


Figure 3-11. 1999 Dry SO_2 Deposition (as S) (kg/ha)

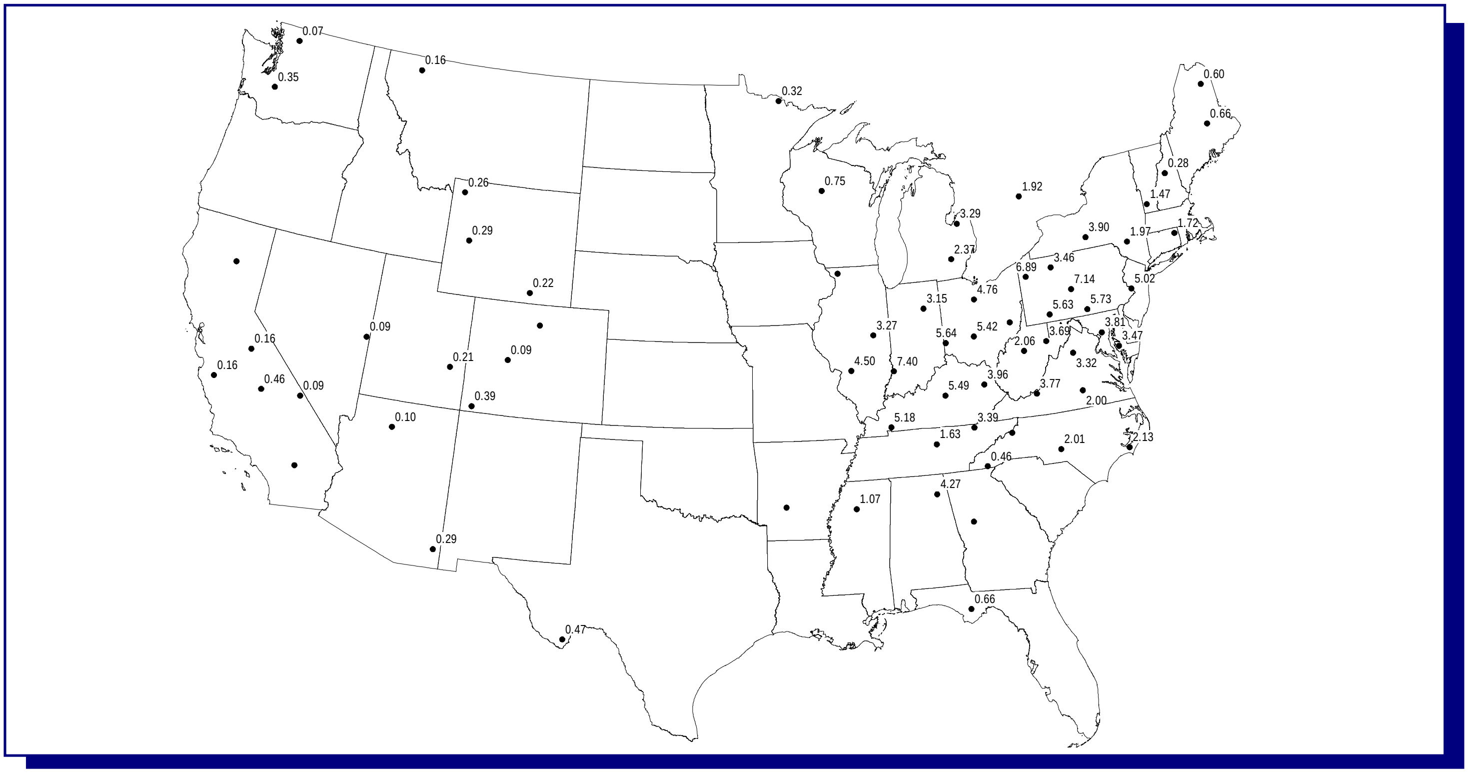


Figure 3-12. 1999 Dry SO_4^{2-} Deposition (as S) (kg/ha)

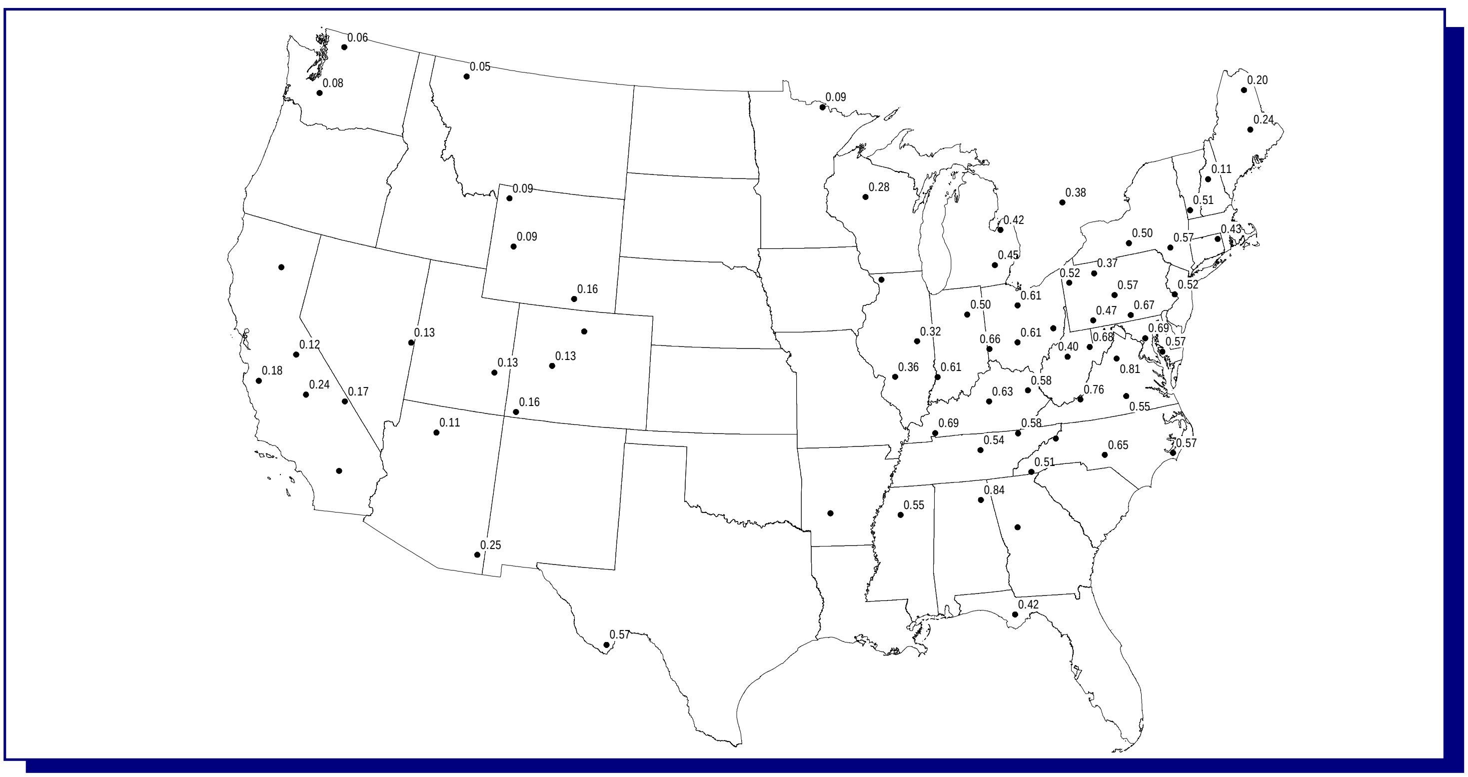
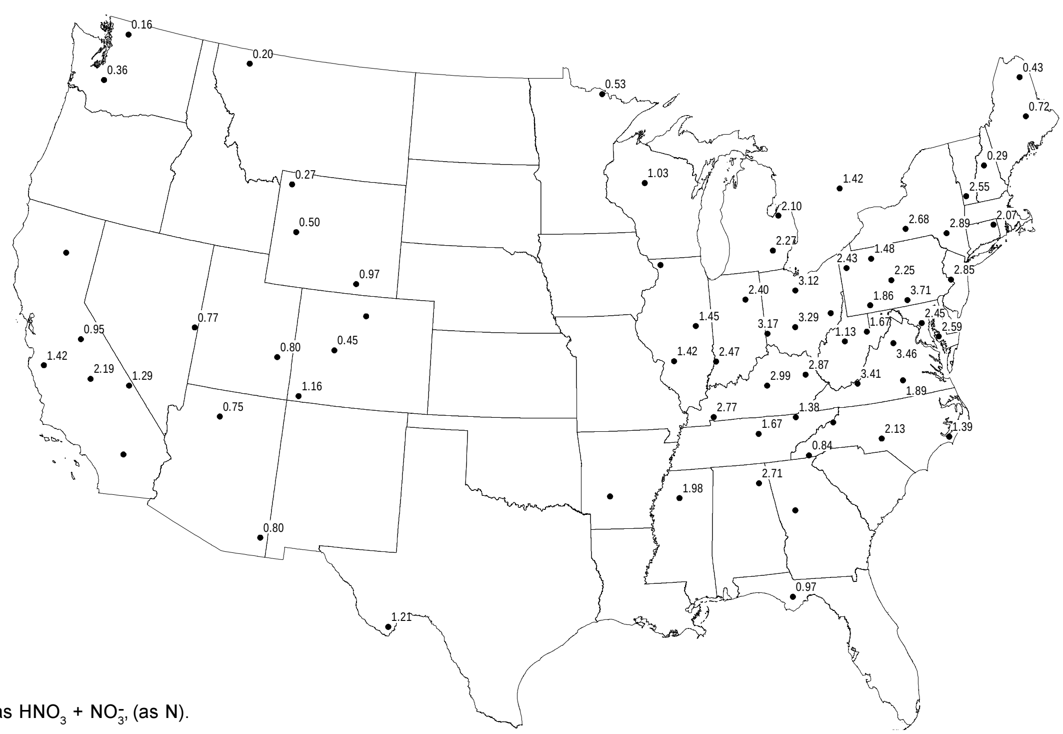


Figure 3-13. 1999 Percentage of Total Dry Sulfur Deposition from SO_2

Figure 3-14. 1999 Total Dry Nitrate Deposition (as N) (kg/ha)



Note:
Nitrate is defined as $HNO_3 + NO_3^-$ (as N).

Figure 3-15. 1999 Dry HNO_3 Deposition (as N) (kg/ha)

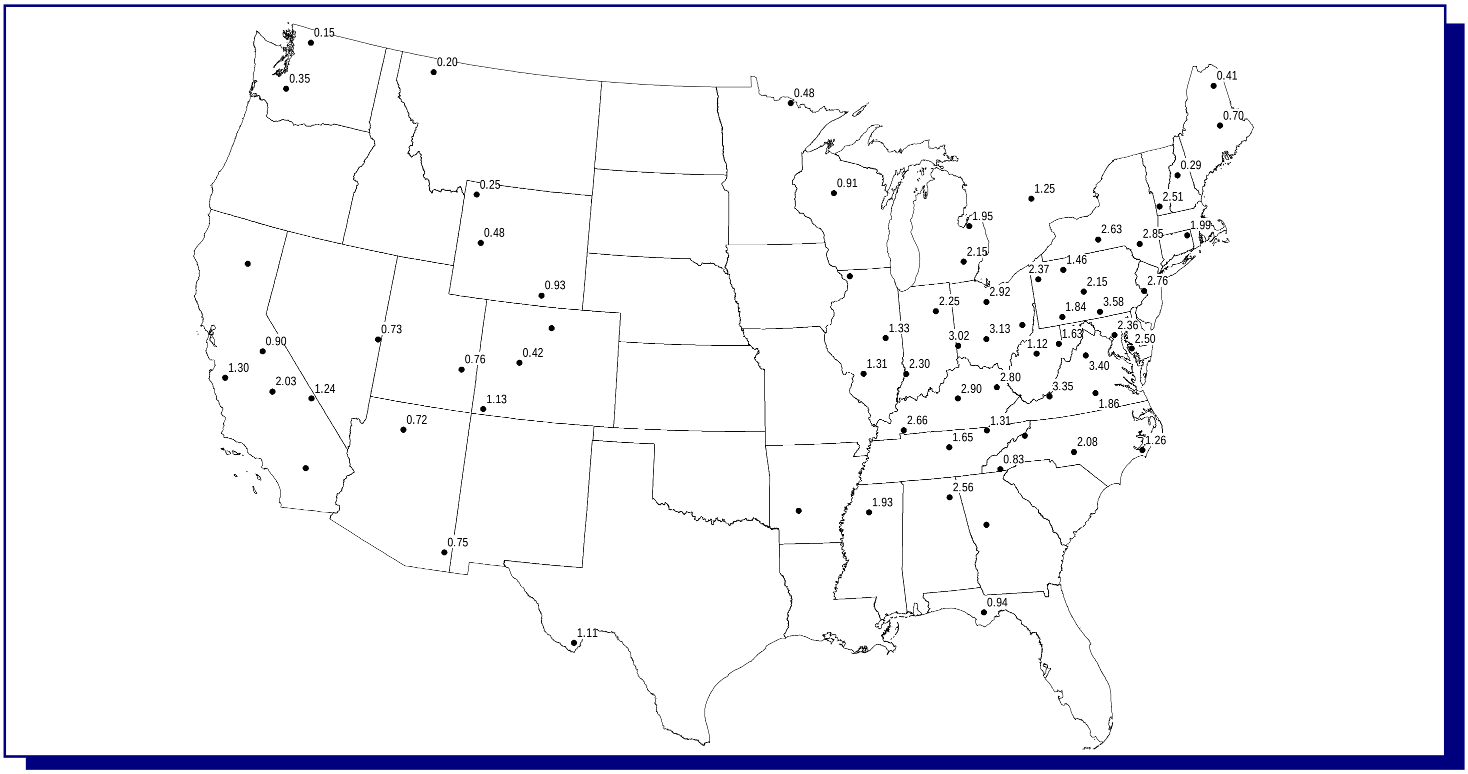


Figure 3-16. 1999 Dry NO_3^- Deposition (as N) (kg/ha)

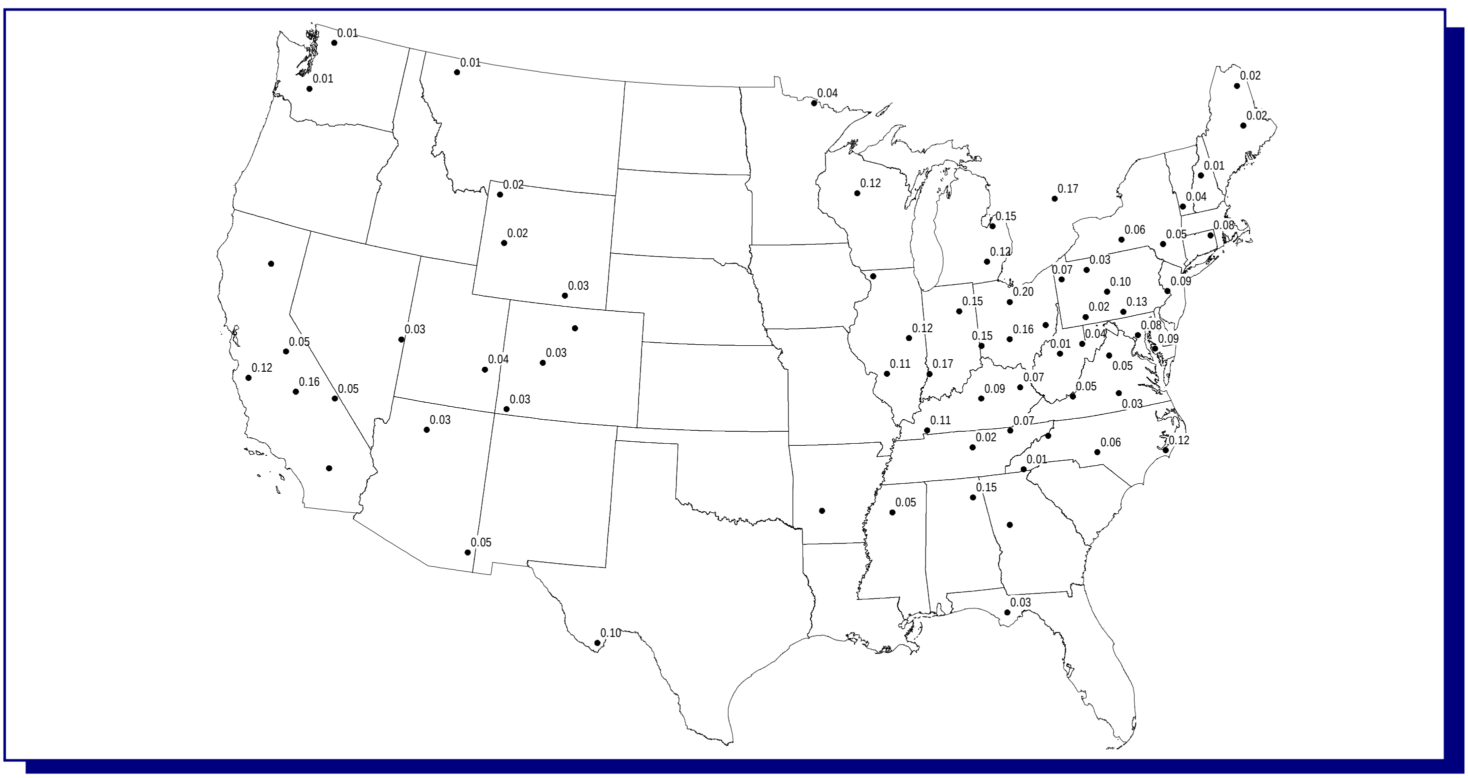


Figure 3-17. 1999 Percentage of Total Dry Nitrate Deposition (as N) from HNO_3

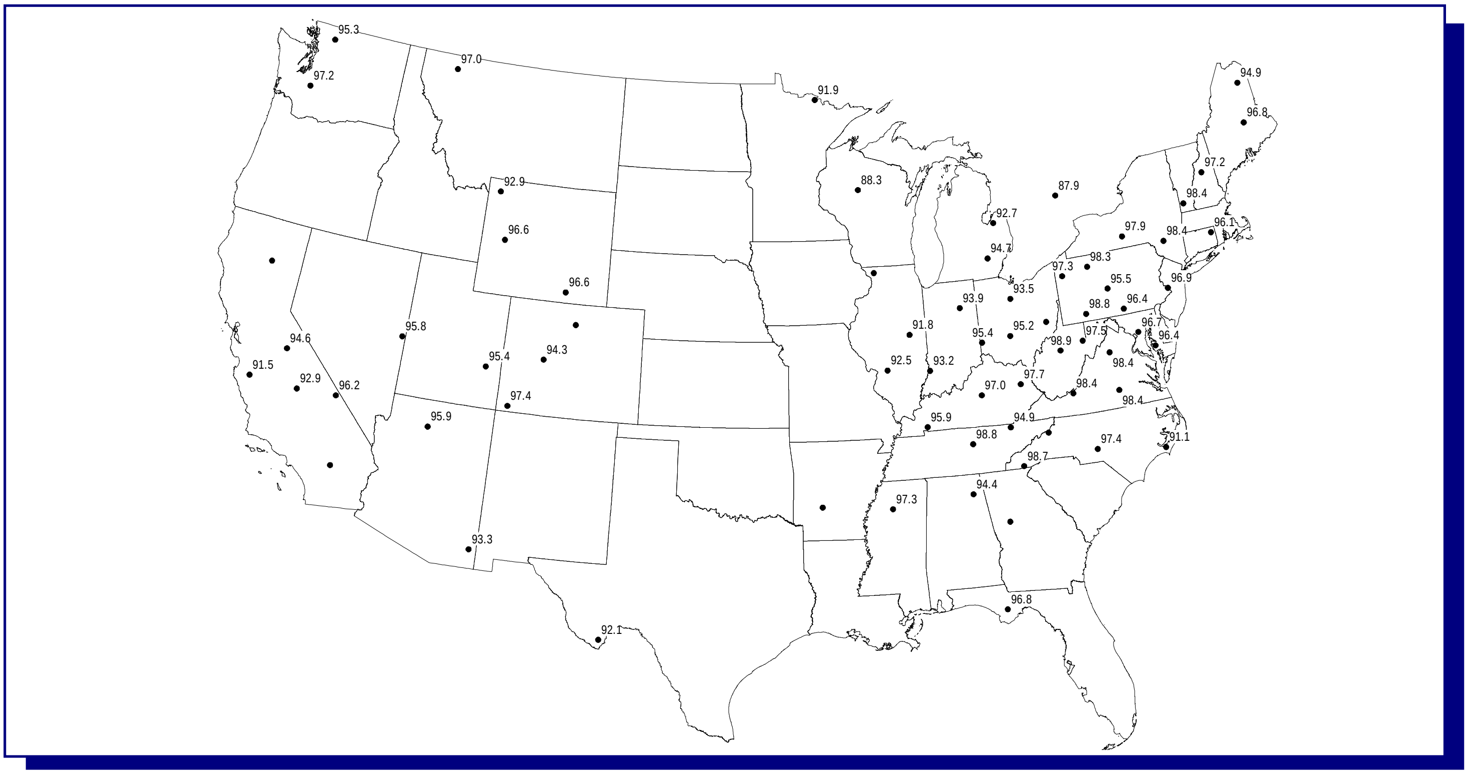


Figure 3-18. 1999 Wet SO_4^{2-} Deposition (as S) (kg/ha)

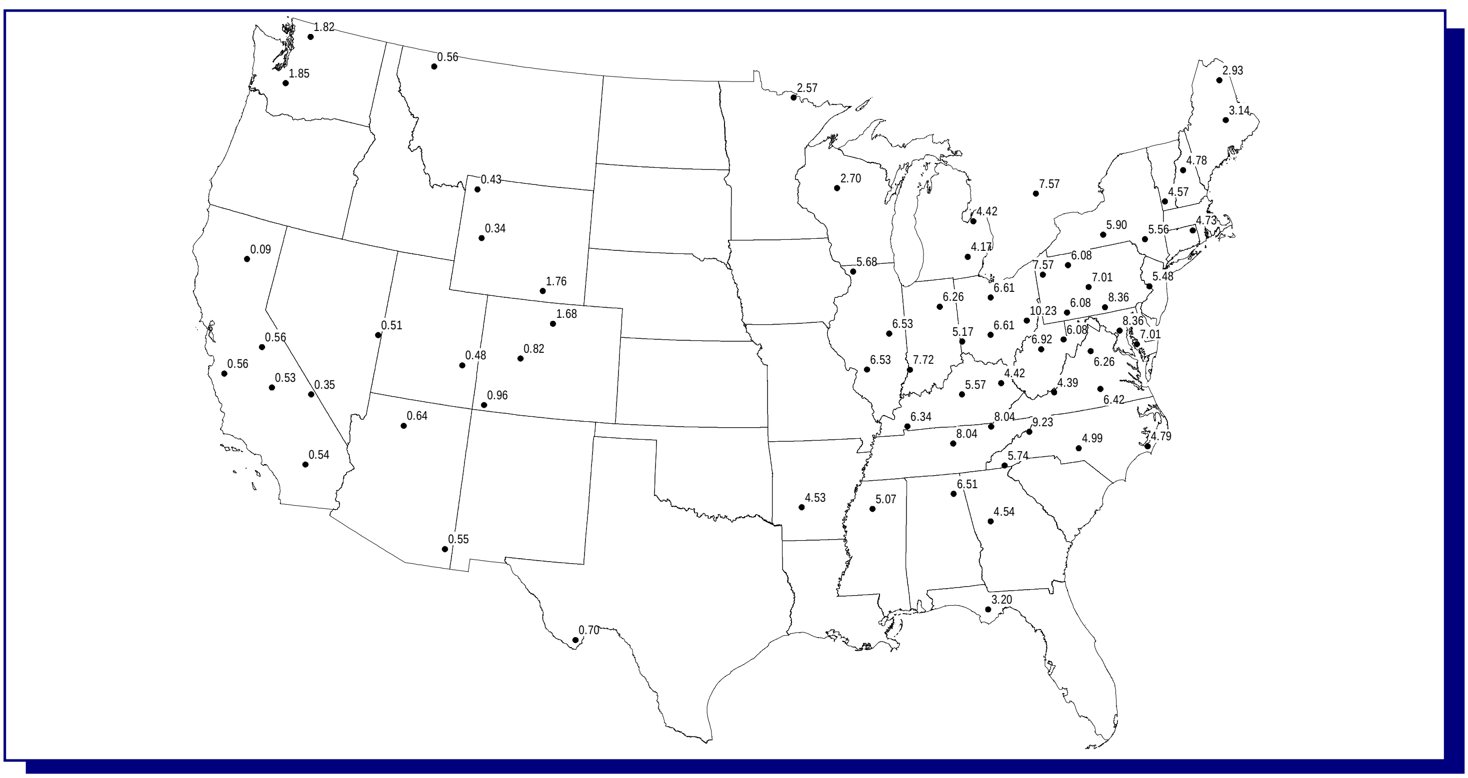


Figure 3-19. 1999 Wet NO_3^- Deposition (as N) (kg/ha)

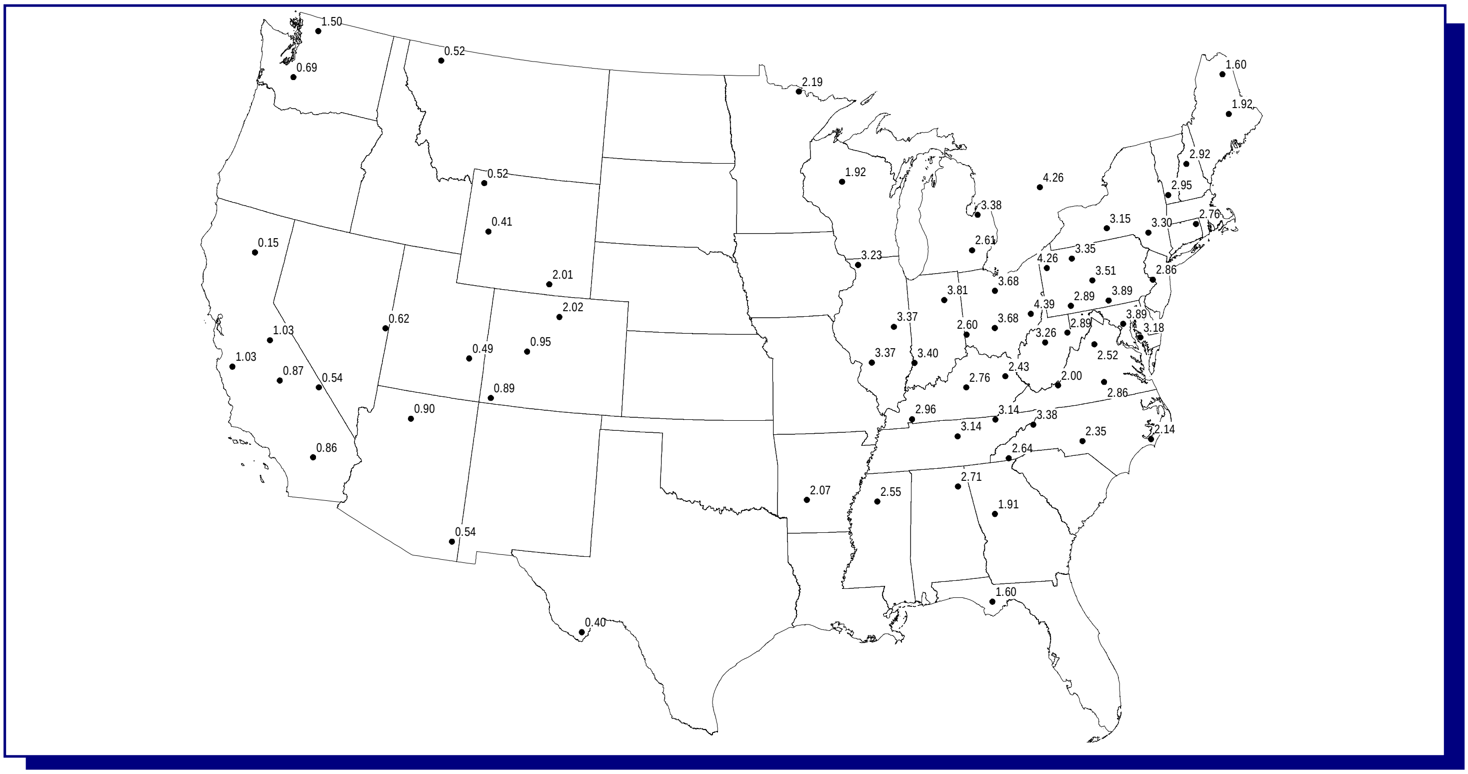


Figure 3-20. 1999 Total Sulfur Deposition (kg/ha)

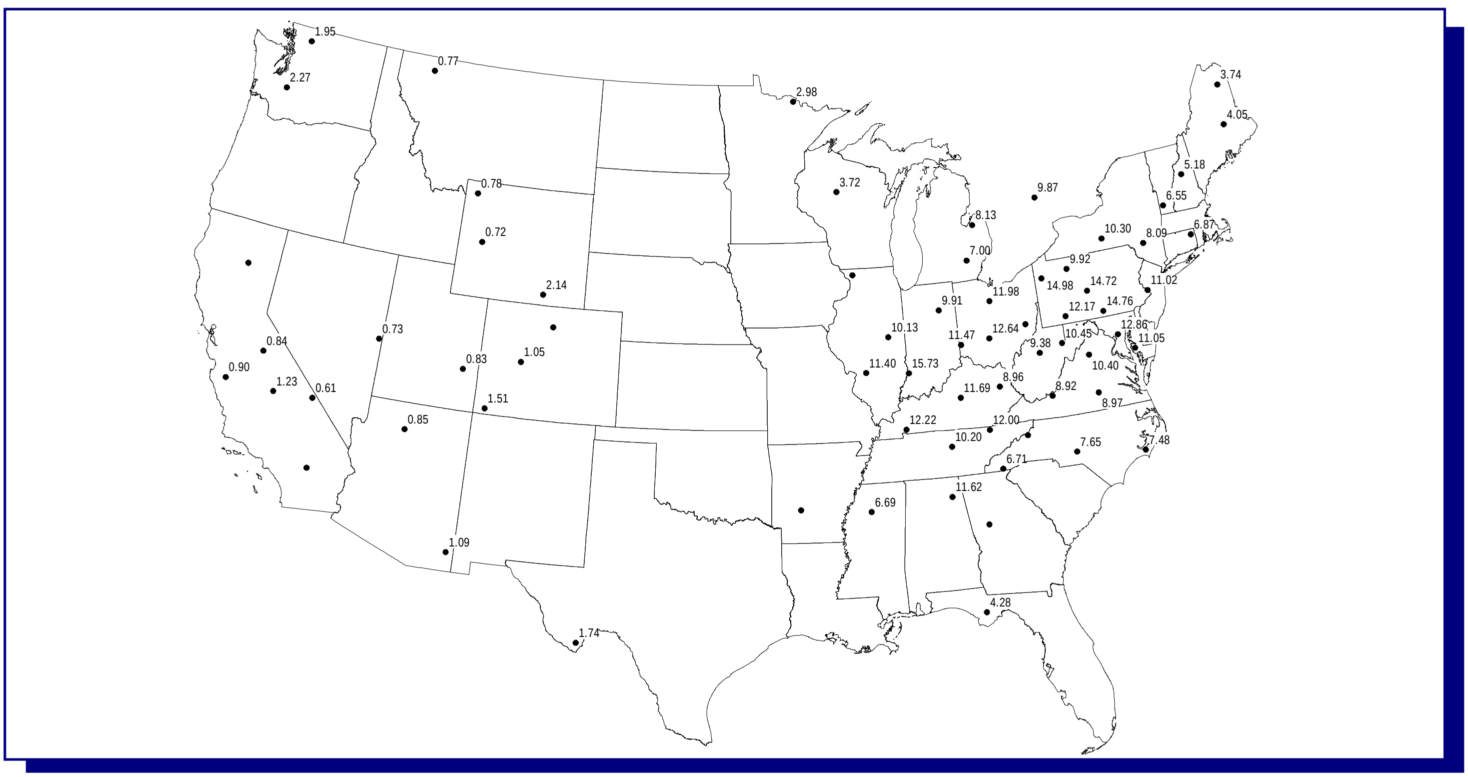


Figure 3-21. 1999 Ratio of Dry Sulfur Deposition to Total Sulfur Deposition

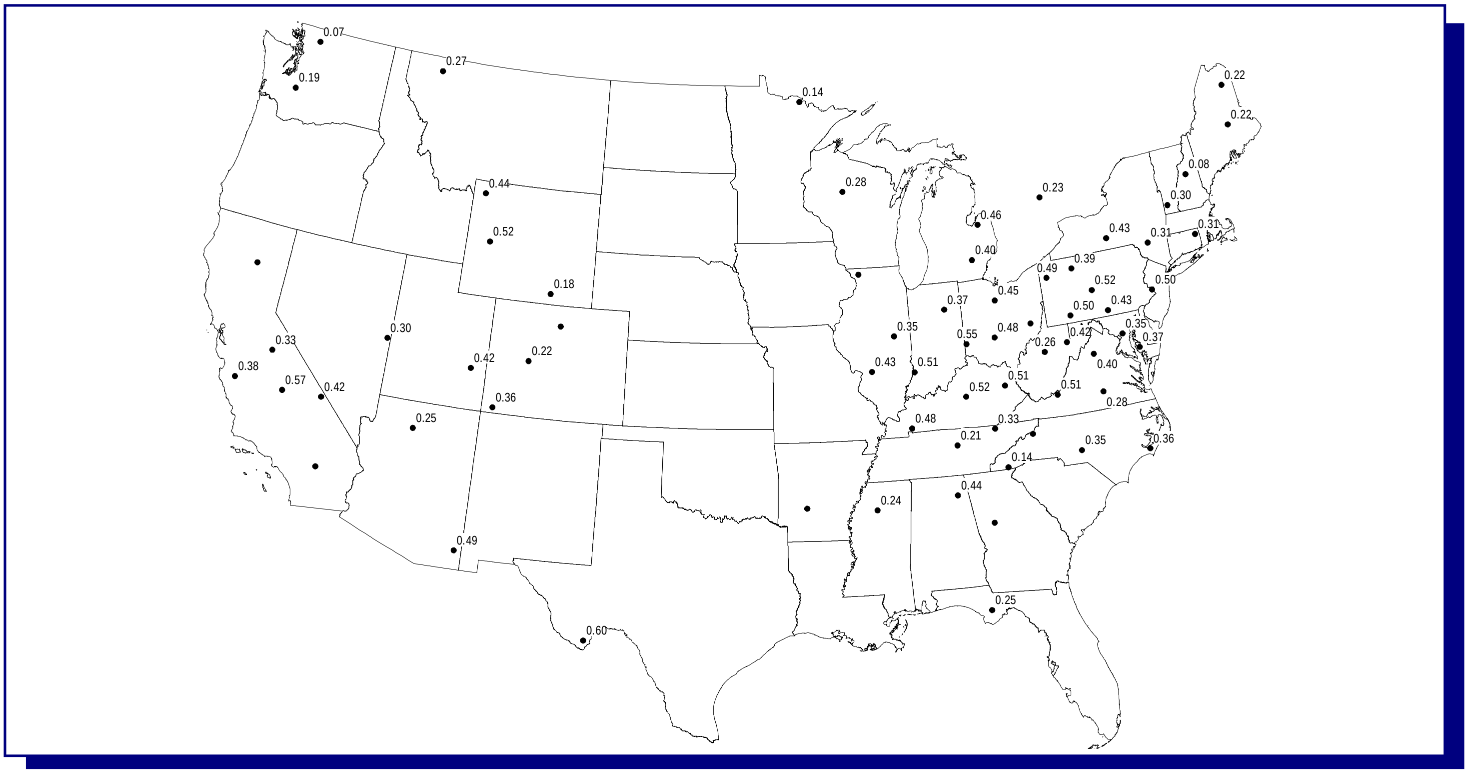


Figure 3-22. 1999 Total Nitrate Deposition (as N) (kg/ha)

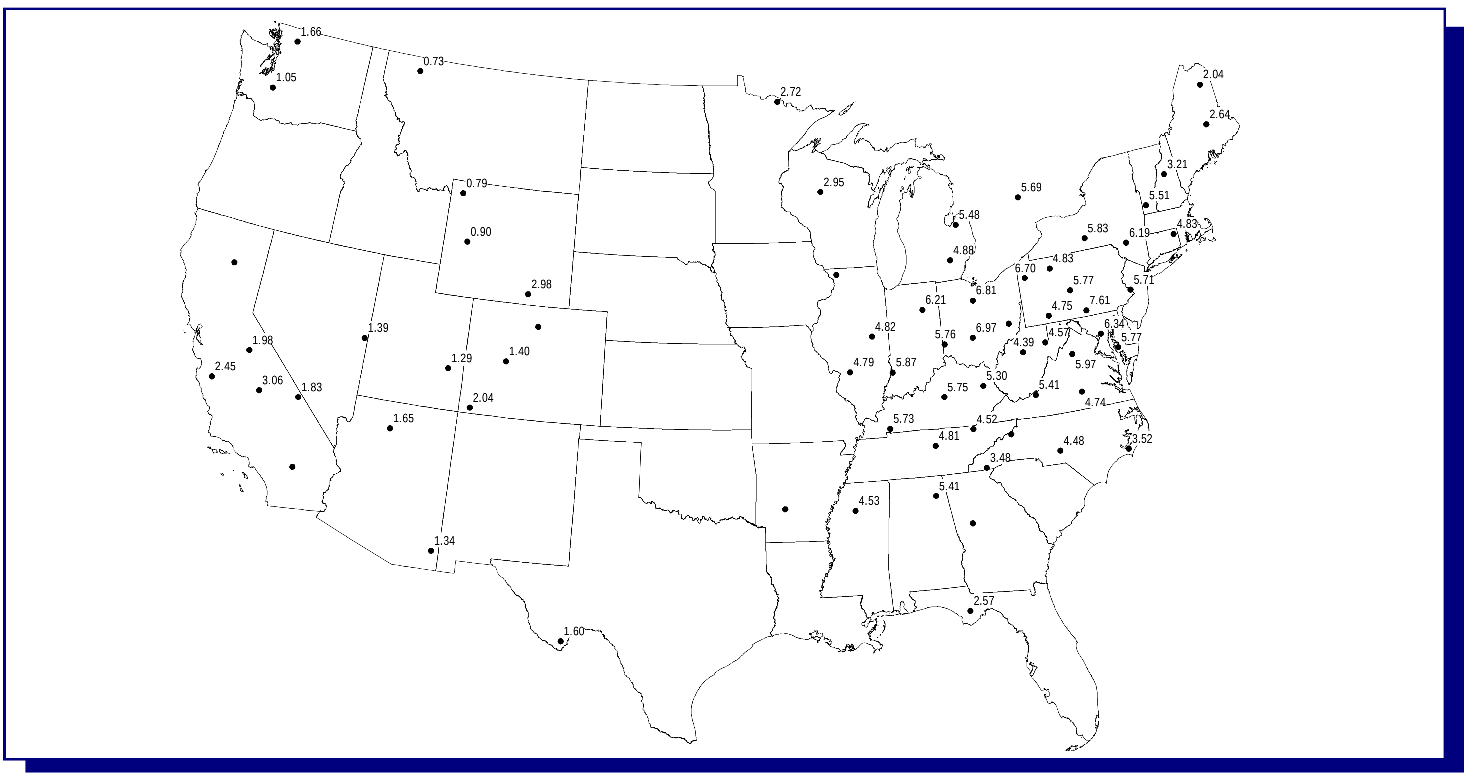


Figure 3-23. 1999 Ratio of Dry Nitrate Deposition to Total Nitrate Deposition

Figure 3-24. Trend in Annual Total Dry Sulfur Deposition

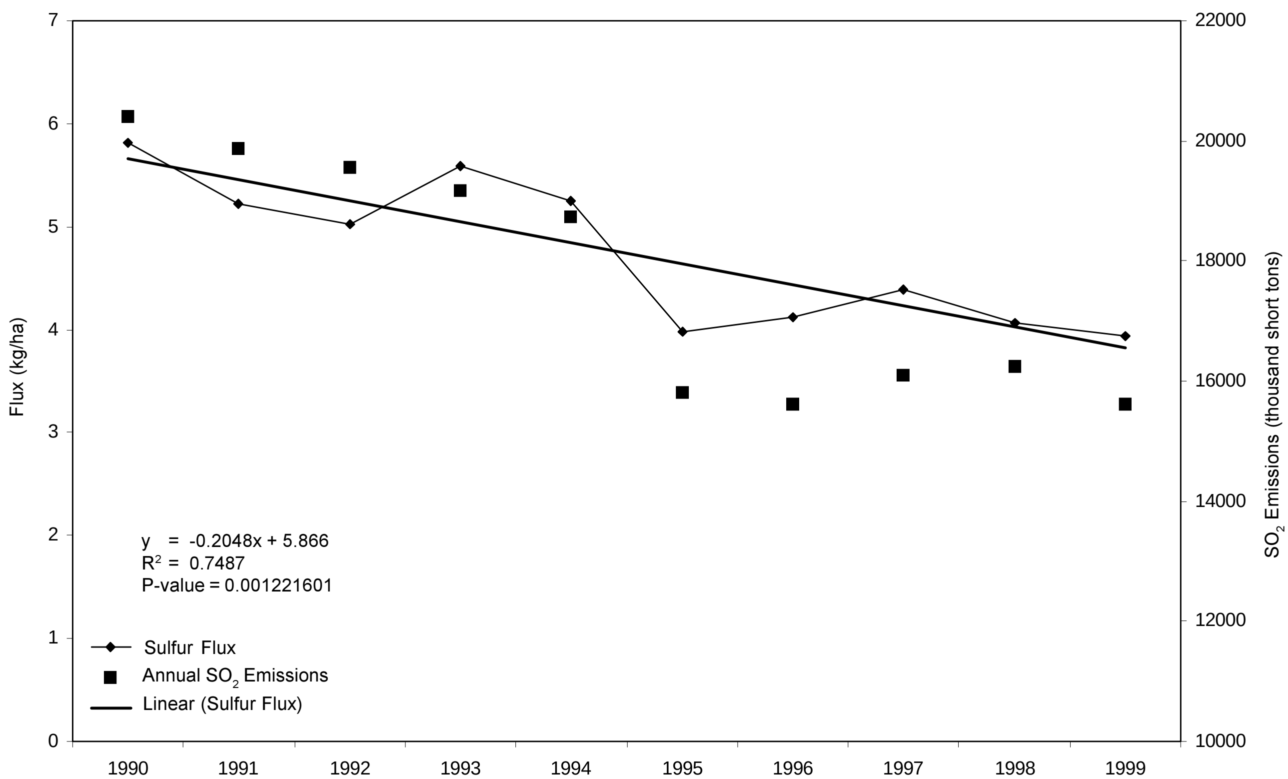


Figure 3-25. Trend in Annual Total Dry Nitrate Deposition (as N)

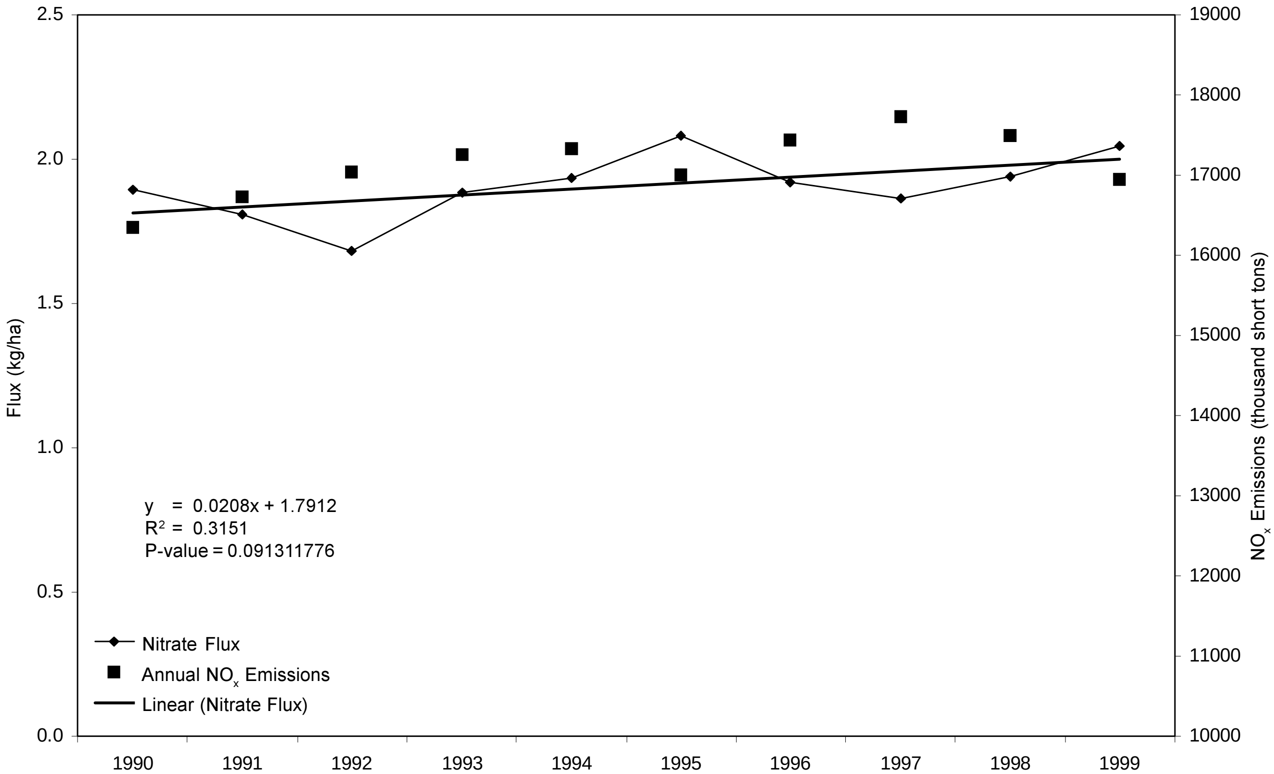


Figure 3-26. Trend in Annual Wet Sulfate Deposition (as S)

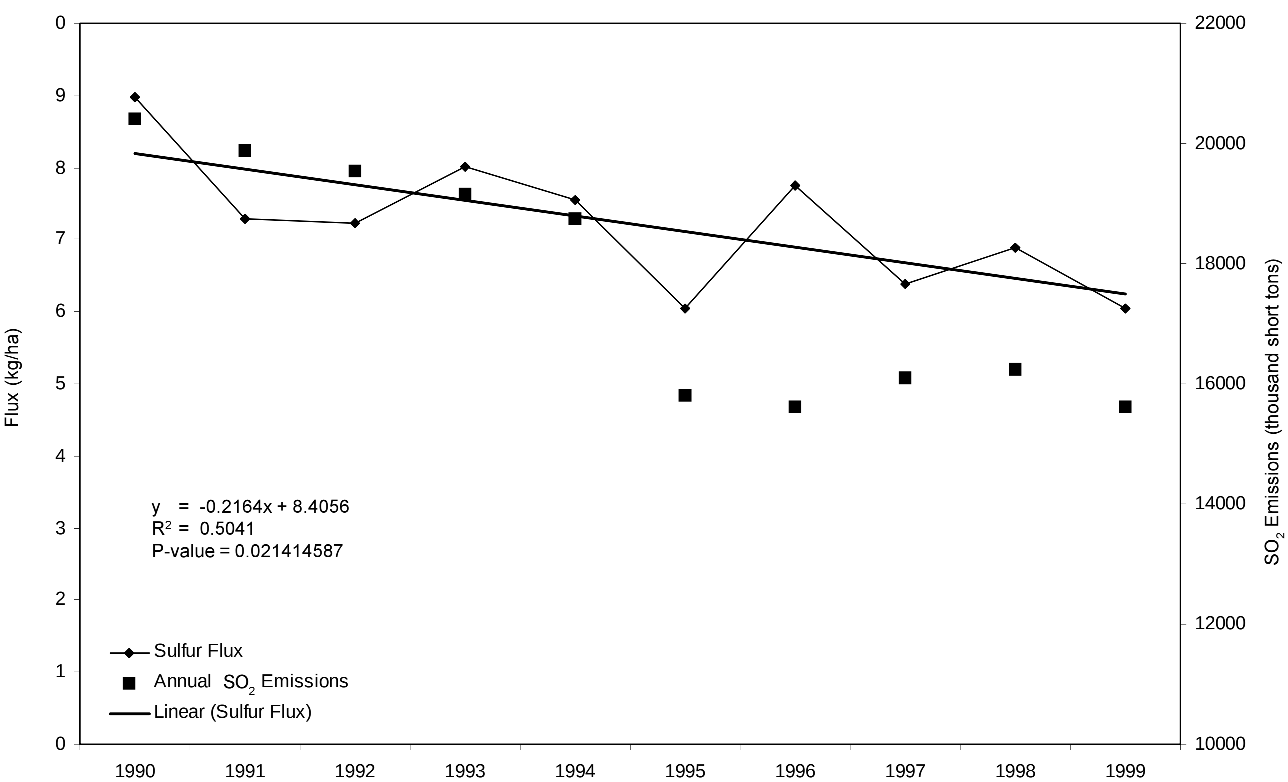


Figure 3-27. Trend in Annual Wet Nitrate Deposition (as N)

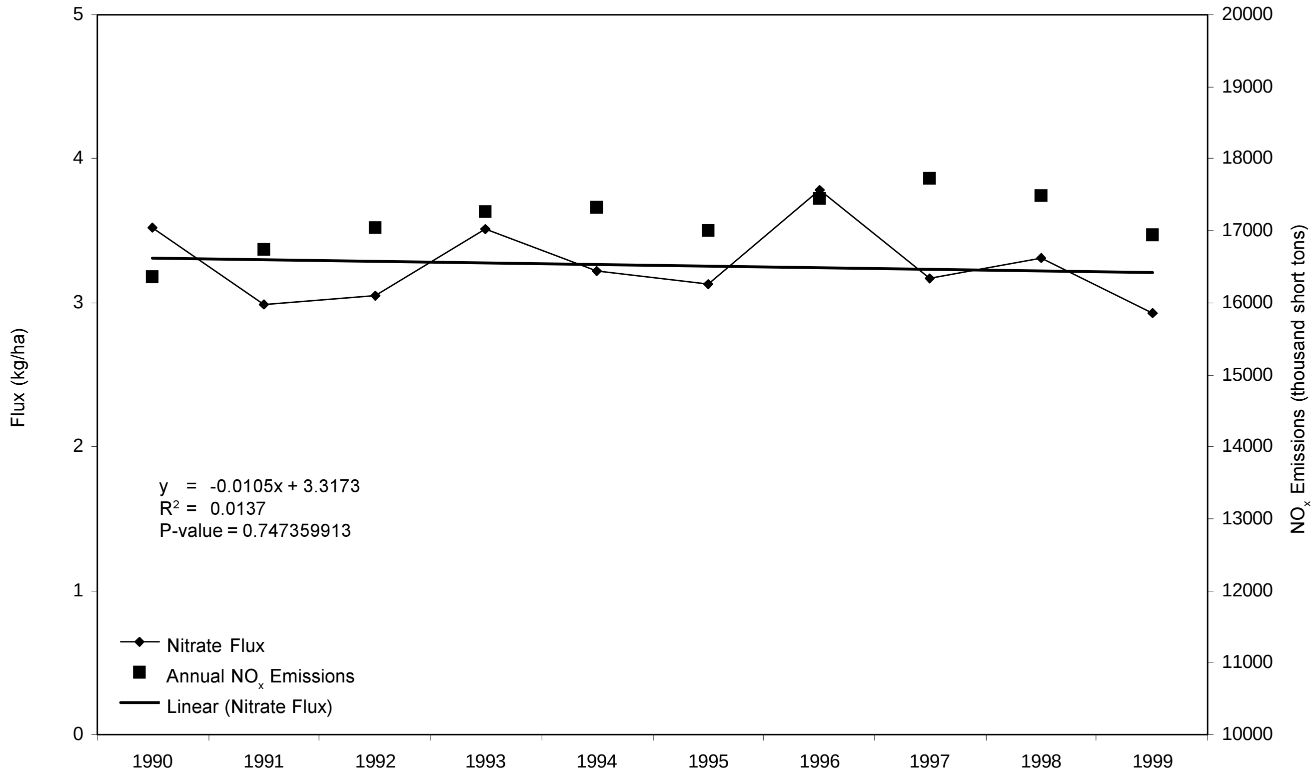


Figure 3-28. Trend in Annual Total Sulfur Deposition

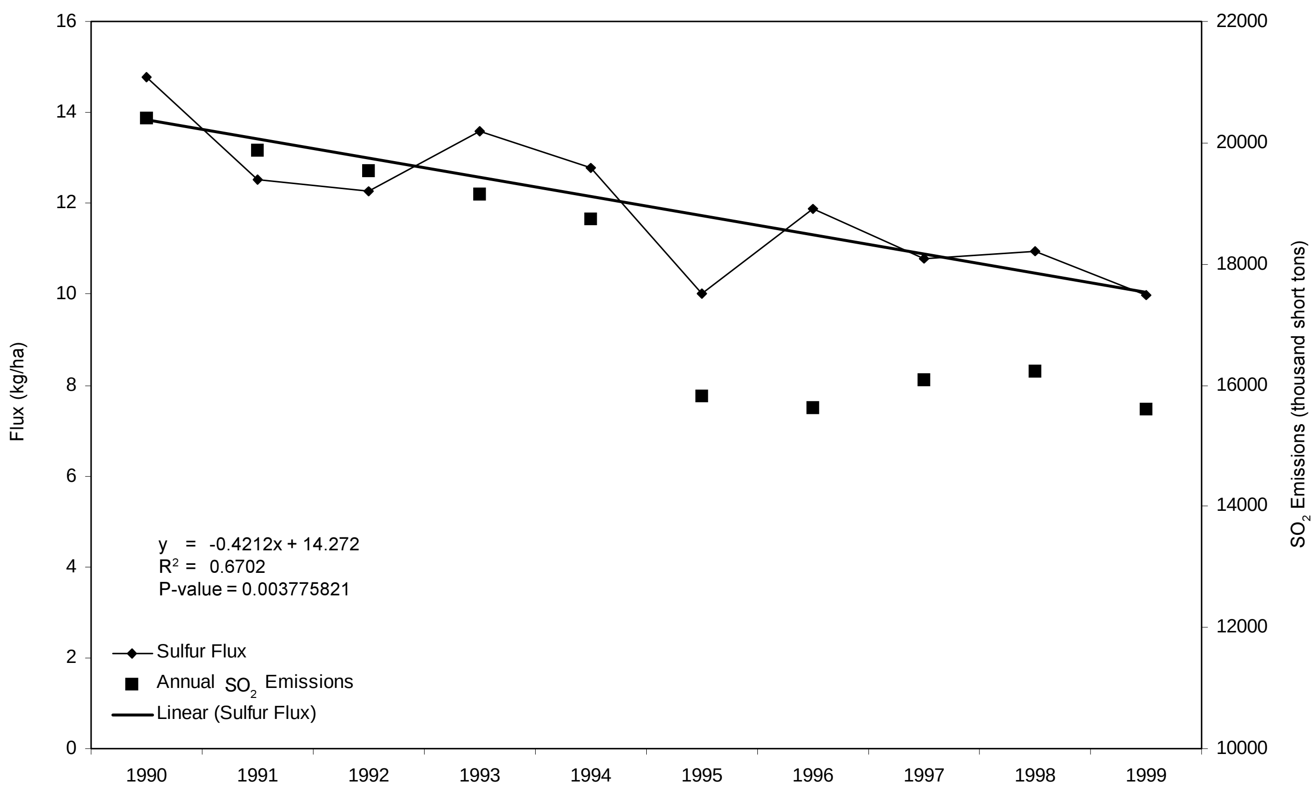


Figure 3-29. Trend in Annual Total Nitrate Deposition (as N)

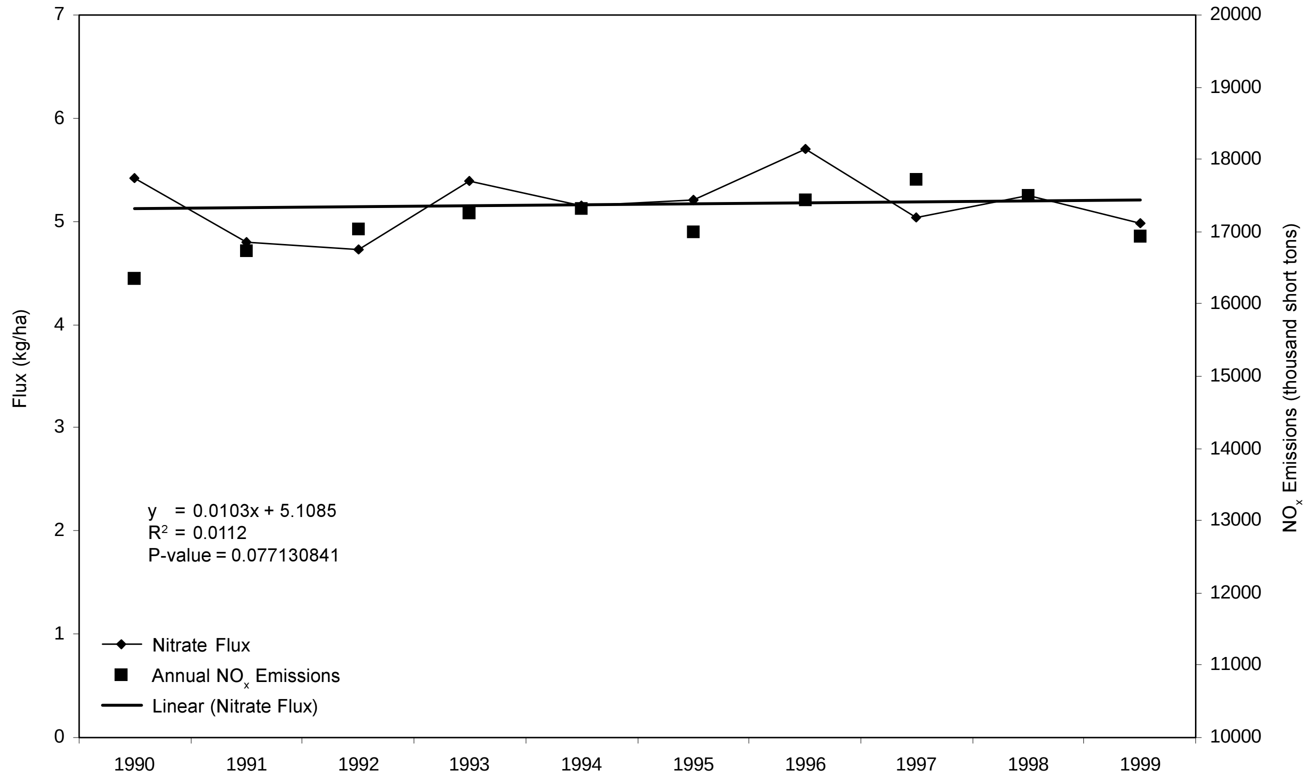


Figure 3-30. Total Sulfur Deposition - 1990 - 1999

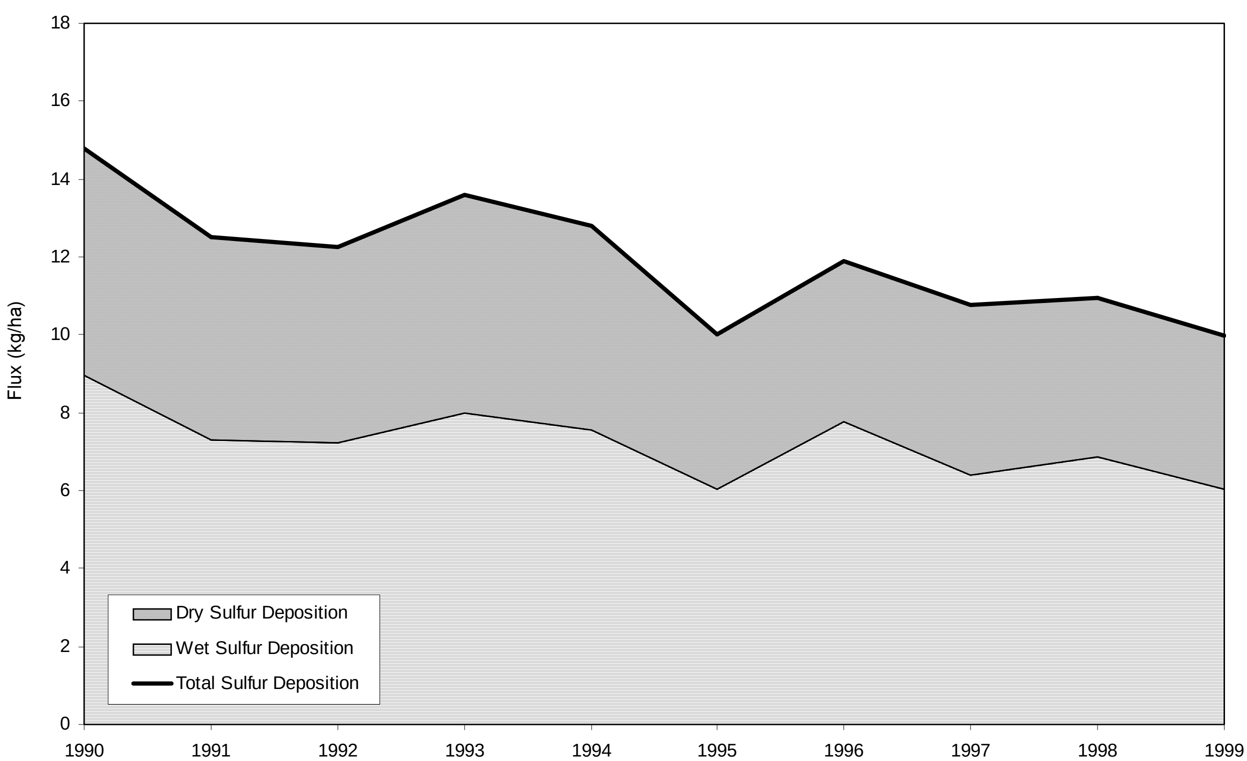


Figure 3-31. Total Nitrate Deposition (as N) - 1990 - 1999

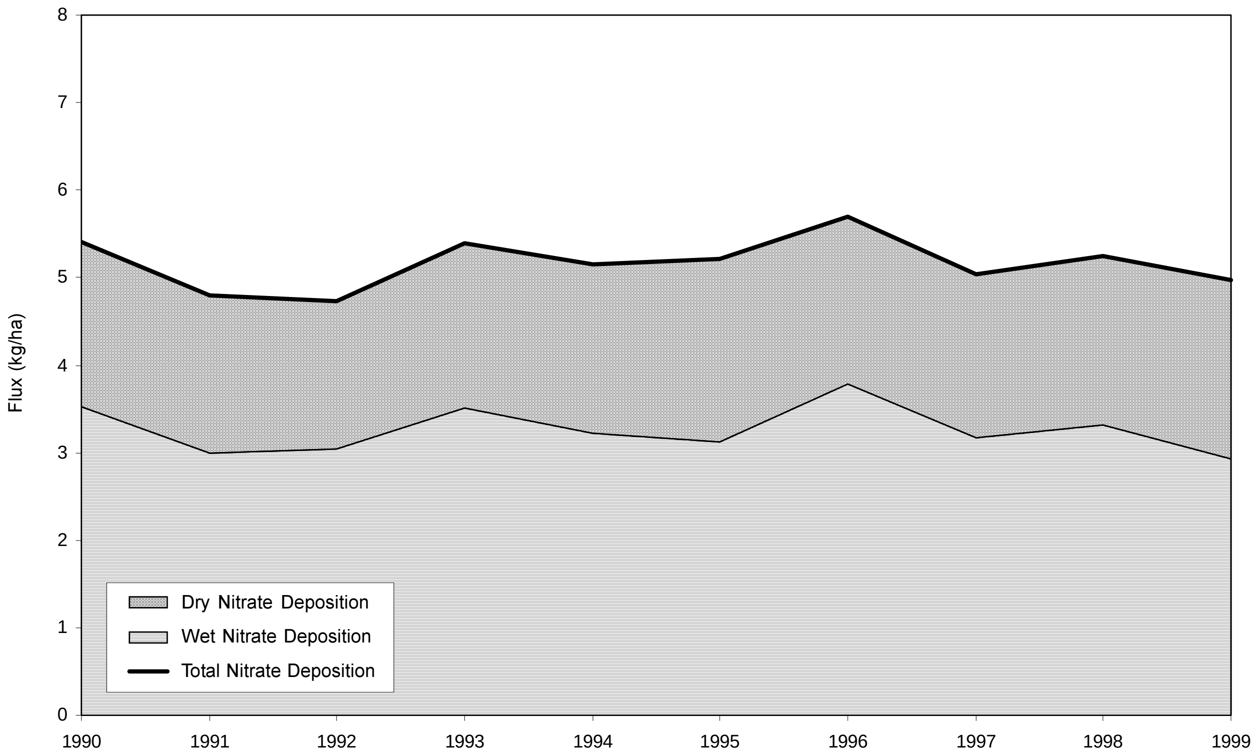


Figure 3-32. Trend in Percent of Total Deposition from Dry Deposition

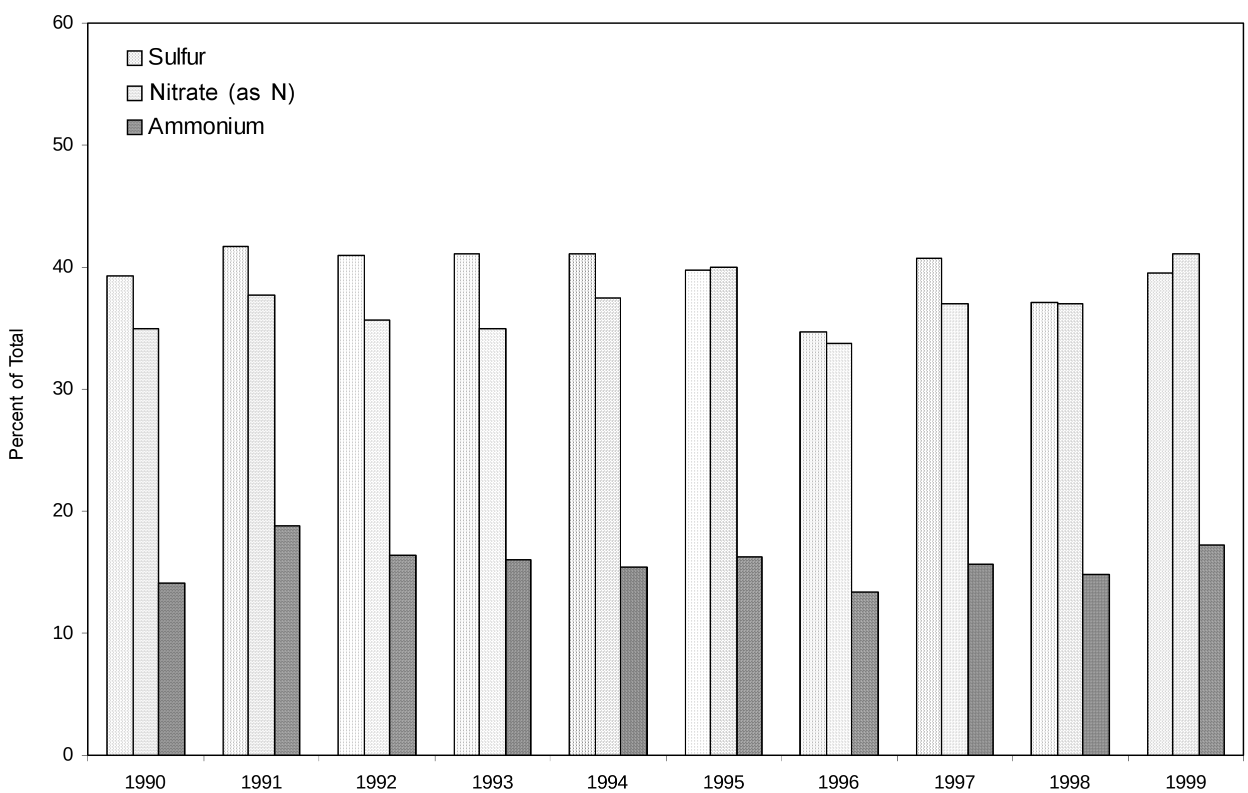


Table 3-1. Annual Average Deposition Velocities* for SO_2 and HNO_3

Region	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
SO_2										
Allegheny Front	0.436	0.374	0.418	0.395	0.409	0.399	0.523	0.414	0.424	0.378
Allegheny Plateau	0.368	0.338	0.363	0.354	0.383	0.343	ins	0.375	0.348	0.335
Mid-Appalachians	0.343	0.292	0.340	0.313	0.327	0.309	0.422	0.324	0.319	0.300
Midwest	0.327	0.338	0.329	0.335	0.325	0.328	0.259	0.325	0.348	0.338
Ohio River Valley	0.427	0.392	0.415	0.424	0.390	0.418	0.430	0.434	0.418	0.380
South	0.334	0.322	0.325	0.328	0.357	0.346	0.363	0.340	0.315	0.311
Unique	0.270	0.265	0.270	0.262	0.282	0.273	0.239	0.270	0.259	0.264
All Eastern Sites	0.344	0.316	0.339	0.336	0.358	0.346	0.358	0.353	0.347	0.327
All Western Sites	0.228	0.216	0.224	0.238	0.234	0.253	0.232	0.234	0.234	0.216
HNO_3										
Allegheny Front	1.300	1.250	1.146	1.251	1.175	1.256	1.272	1.266	1.253	1.254
Allegheny Plateau	1.215	1.243	1.271	1.304	1.301	1.403	ins	1.335	1.278	1.335
Mid-Appalachians	1.168	1.114	1.164	1.176	1.167	1.167	1.251	1.245	1.174	1.266
Midwest	1.059	0.953	1.099	1.070	1.119	1.129	1.326	1.132	1.140	1.162
Ohio River Valley	1.288	1.304	1.313	1.394	1.363	1.358	1.387	1.415	1.345	1.428
South	1.268	1.280	1.248	1.337	1.335	1.474	1.515	1.389	1.339	1.343
Unique	1.120	1.069	1.074	1.079	1.116	1.184	1.049	1.139	1.111	1.154
All Eastern Sites	1.190	1.151	1.190	1.236	1.292	1.332	1.293	1.312	1.306	1.323
All Western Sites	1.406	1.518	1.477	1.509	1.493	1.556	1.551	1.468	1.506	1.390

Note: ins = Insufficient data: a site must have 8 valid samples per quarter and 3 valid quarters per year to be included in summary statistics.

* All values in cm/sec.

Table 3-2. Annual Average Deposition Velocities* for Ozone and Particles

Region	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
Ozone										
Allegheny Front	0.189	0.164	0.170	0.179	0.170	0.178	0.159	0.160	0.163	0.160
Allegheny Plateau	0.187	0.179	0.187	0.164	0.190	0.197	ins	0.179	0.184	0.168
Mid-Appalachians	0.208	0.174	0.212	0.186	0.186	0.190	0.204	0.193	0.198	0.180
Midwest	0.150	0.126	0.147	0.146	0.146	0.159	0.136	0.146	0.148	0.142
Ohio River Valley	0.192	0.170	0.188	0.181	0.171	0.195	0.191	0.189	0.194	0.164
South	0.175	0.198	0.179	0.176	0.194	0.204	0.193	0.179	0.181	0.172
Unique	0.182	0.179	0.177	0.167	0.189	0.186	0.177	0.174	0.153	0.173
All Eastern Sites	0.182	0.172	0.180	0.172	0.187	0.193	0.185	0.178	0.186	0.173
All Western Sites	0.124	0.127	0.123	0.128	0.120	0.122	0.135	0.131	0.133	0.133
Particles										
Allegheny Front	0.097	0.098	0.079	0.096	0.086	0.093	0.101	0.095	0.107	0.099
Allegheny Plateau	0.098	0.103	0.099	0.103	0.106	0.116	ins	0.106	0.103	0.111
Mid-Appalachians	0.098	0.096	0.096	0.099	0.102	0.104	0.098	0.110	0.103	0.116
Midwest	0.085	0.079	0.085	0.083	0.094	0.094	0.113	0.091	0.096	0.102
Ohio River Valley	0.104	0.104	0.102	0.108	0.115	0.111	0.115	0.115	0.109	0.122
South	0.110	0.106	0.103	0.115	0.113	0.129	0.131	0.119	0.113	0.117
Unique	0.097	0.089	0.091	0.089	0.093	0.102	0.090	0.094	0.090	0.096
All Eastern Sites	0.099	0.096	0.096	0.101	0.108	0.114	0.109	0.109	0.109	0.114
All Western Sites	0.143	0.152	0.149	0.148	0.150	0.171	0.155	0.148	0.149	0.140

Note: ins = Insufficient data: a site must have 8 valid samples per quarter and 3 valid quarters per year to be included in summary statistics.

* All values in cm/sec.